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ENVIRONMENTAL ASSESSMENT: SOURCE TEST AND EVALUATION REPORT -
RECTISOL ACID GAS REMOVAL

TRW Inc.
Redondo Beach, CA

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ENVIRONMENTAL ASSESSMENT: SOURCE TEST AND
EVALUATION REPORT - RECTISOL ACID GAS REMOVAL

By

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TRW Inc.
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ABSTRACT

In June of 1982, the Industrial Environmental Research Laboratory of EPA at Research Triangle Park, North Carolina sponsored a field test of a Rectisol acid gas removal unit at a Texaco refinery at Wilmington, California. The primary goal of this test was to provide a data base for evaluation of Rectisol performance in entrained coal gasification applications. Currently the only Rectisol units operating in coal gasification applications are outside the USA. Therefore, the unit at Wilmington was selected for testing. This Rectisol processes gases from the partial oxidation (POX) of oil by the Texaco Synthesis Gas Generation Process, and its design is similar to at least one Rectisol planned for a U.S. coal gasification facility. A secondary goal of the subject test was to validate sampling/analytical methods for constituents such as HCN and NH_3 which were expected to be present at low levels in the Wilmington gas samples.

During the test period, the Rectisol unit handled a feed gas containing about 0.2% H_2S , a few ppmv COS, and over 30% CO_2 and generated a product gas containing less than 0.1 ppmv total sulfur and usually less than 200 ppmv CO_2 . Over 99.8% of the total sulfur entering the Rectisol was found in the H_2S -rich gas which is sent to the refinery Claus plant. The sulfur loading of the H_2S -rich fraction (about 15% by volume) was lower than design due primarily to the relatively low level of sulfur in the heavy oil used as POX feed during the test period. CO_2 -rich offgases from the Rectisol unit contained less than 10 ppmv total sulfur consistent with both the original design and existing local air pollution control regulations for this source type.

With regard to minor constituents, the CO_2 -rich offgases contained about 400-900 ppmv of methanol (derived from the process solvent), less than 1 ppmv of hydrocarbons other than methane and ethane, and less than 1 ppmv each of HCN or NH_3 . The latter two species were only found at low levels in the feed gas, presumably due to the effects of shift conversion and moisture removal.

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which precede this Rectisol. Due to their absence in the vacuum residual oil feed to the POX unit, no detectable amounts of volatile heavy elements (e.g., Hg, As, Se) were found in Rectisol gases.

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The test data substantially confirm the previously reported environmental performance capabilities of the subject and other Rectisol units currently in coal gasification service. The data from the test are further evaluated in this report from the standpoint of differences in feed gas composition which would be encountered in coal vs. oil applications and/or where only part of the gas is shifted. Based on the review and extensive comments from the process vendor, Linde, A.G. (W. Germany), a number of design variations are discussed which would address these differences in feed characteristics, product gas specifications, and constraints on direct atmospheric discharges.

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ACKNOWLEDGEMENT

The authors would like to express their appreciation to the personnel of Texaco, Inc., Lotepro Corp., and Linde, A.G., who devoted their time and efforts to make this test a success. The operations staff at the Wilmington refinery were more than cooperative with the EPA program, providing the test crew with much needed assistance both prior to and during the test. Special thanks go to Dr. Volker Mohr of Lotepro and Dr. Warren Schlinger of Texaco who were instrumental in arranging for the conduct of the test, and to Dr. Heinz Karwat and Dr. Garhard Ranke of Linde for their review of and assistance in the interpretation of the data.

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INTRODUCTION

EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina (IERL-RTP), is responsible for the Agency's environmental assessment activities and for control technology development research relating to substitute fuels from coal. Part of the assessment activities involve generation of background data on the characteristics of waste streams generated by coal gasification and associated technologies and evaluation of the performance of control technologies for such waste streams. IERL-RTP assessment programs involve three general areas of effort: (1) collection and evaluation of existing process and environmental data, (2) acquisition of supplementary data through sampling and analysis of selected process/waste streams at domestic or foreign facilities, and (3) environmental assessment and necessary process engineering support studies.

Although emphasis in EPA-sponsored data collection activities has focused mainly on gasification processes, it has also been apparent that significant data gaps exist regarding processes downstream of gasification. These downstream processes have a major influence on potential wastes generated in integrated coal gasification facilities. The Rectisol process(es) is a prime candidate for removal of acid gases from Lurgi, Texaco, and Koppers-Totzek gasifier products, and most proposed U.S. gasification facilities feature the process(es) in their designs.

The proposed widespread use of Rectisol in U.S. coal gasification facilities and the importance of removed acid gas as potential atmospheric emissions from such facilities prompted EPA to investigate a test program at an existing unit. Currently, the only Rectisol units operating in coal gasification applications are outside the U.S. However, two units exist in the U.S. which process gases from the Texaco synthesis gas generation process (partial oxidation

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or POX) of heavy oil. After exploring both overseas and domestic units, the Rectisol at Texaco's Wilmington refinery was selected for testing. Although this unit processes shifted gas from oil rather than coal gasification, the design is similar to at least one planned for a U.S. coal gasification facility, and hence the data for this unit can be useful for assessment of coal-based units. Texaco Development Corporation, Manufacturing Dept. of Texaco, USA, and Lotepro Corporation (a subsidiary of Linde A.G. of Munich, W. Germany) agreed to cooperate with EPA in the testing of this unit, with the actual on-site test work contracted to TRW, Inc.

The goals of the Wilmington Rectisol test were threefold. Primarily, the test was conducted to evaluate the performance of the specific unit from an environmental standpoint via characterization of both process and waste streams for a variety of species of environmental interest. In addition, the test was to establish the applicability of key sampling and analytical techniques as applied to the matrices of Rectisol streams. Finally, the test data were to serve as a partial basis for estimating the environmental effects of Rectisol units in coal gasification applications, with inputs from Lotepro and Texaco providing guidance in this data extrapolation.

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SECTION 2

DESCRIPTION OF THE FACILITY

The Rectisol unit at the Texaco refinery in Wilmington, California, designed and built by Linde A.G. of Munich, West Germany,* is part of a hydrogen production train referred to as the hydrogen generation unit (HGU). The HGU, based upon gasification of vacuum residual oil to generate synthesis gas, provides a part of the hydrogen used in the refinery. The Texaco partial oxidation (POX) gasifier generates a hot crude gas containing about 43% H_2 , 50% CO , 5% CO_2 , 0.5% H_2S plus COS , and entrained soot consisting primarily of ungasified carbon (1). The soot is removed by water washing in a carbon scrubber which also serves to cool the gas and recover heat. Soot is recovered from the soot-water mixture in a separate unit by contacting with naphtha (2). Dust free, cooled gas is fed at about 230°C and 3.4 MPa to a sour (sulfur tolerant) shift conversion unit. Shifted gas is cooled in stages with steam production and condensate recovery. Cooled condensates are either recycled to the shift reactor or the carbon scrubber or discharged to wastewater treatment. Cooled shifted gas at 43°C and 3.2 MPa is fed to the Rectisol unit for removal of H_2S and CO_2 . For trace CO removal, a copper liquor wash step follows Rectisol.

The Wilmington Rectisol is a high pressure acid gas removal unit with a design capacity of 4000 kmol/hr of throughput (3). The process utilizes cold methanol as a solvent to remove acid gases by physical absorption under pressure, with solvent regeneration by a combination of pressure reduction, stripping with inert gas (N_2), and heating. The wash process was designed to remove $H_2S + COS$ to below 1 ppmv and CO_2 to 10 ppmv and to supply an H_2S fraction with at least 10% H_2S at 0.41 MPa and a CO_2 tailgas with 5 ppmv maximum H_2S . At the time the Wilmington unit was constructed (1965), no specification

* In the United States, services and products of Linde are marketed by Lotepro Corporation of New York (1140 Avenue of the Americas, N.Y., N.Y.) which is a wholly owned subsidiary of Linde Aktiengesellschaft, West Germany.

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was set for COS in CO₂ tailgas. Recent Linde designs call for less than 10 ppmv total sulfur in the tailgases (including less than 5 ppmv H₂S).

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It should be mentioned that the Wilmington Rectisol unit is the first one designed for completely selective removal of H₂S + COS and of CO₂. While results from this unit are relevant to current designs from an environmental point of view, the economics of the Wilmington unit are no longer typical. Modern plants have lower specific energy requirements and the tendency is towards higher operating pressures, higher concentrations of H₂S + COS in the sulfur-rich off-gas, and larger capacities.

Figure 2-1 is a simplified flow diagram of the process indicating streams of interest for environmental testing (4). The feed gas (Stream 1) is cooled against cold separation products, with methanol injection to prevent ice formation. After separation of the condensate (i.e., water plus methanol), H₂S and COS are removed from the gas in the bottom section of the wash tower with CO₂-loaded methanol. Since the methanol is already saturated with CO₂ from the CO₂ absorption section, the only cooling requirements are the heat of solution of the H₂S and the cooling of the gas which are easily met by some warming of the cold methanol solvent with no intermediate cooling. The sulfur-free gas is washed in the top section of the wash tower with a larger quantity of methanol, as determined by the lower solubility of CO₂ compared with H₂S. The warming of the methanol in this section, due to the heat of solution of CO₂ and to cooling of the gas, is such that the partly loaded methanol must be cooled in two intermediate stages with freon refrigerant at -44°C. The gas leaving the top of the wash tower (Stream 2) meets the necessary product purity specifications and, after warming to ambient temperature against the feed gas, is delivered to the copper liquor plant where CO is removed to ppm levels.

The methanol leaving the bottom of the H₂S absorption section contains all of the H₂S and also CO₂ and H₂ in amounts corresponding to their partial pressures and solubilities. Hydrogen recovery is increased from 98% to 99.5% by flashing the loaded methanol to an intermediate pressure and recycling the flash gas (mainly H₂ + CO₂ with some H₂S) back to the feed gas via a small recycle compressor.

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The flashed methanol still contains too much CO₂ to achieve the necessary H₂S concentration and must, therefore, be further flashed and stripped with

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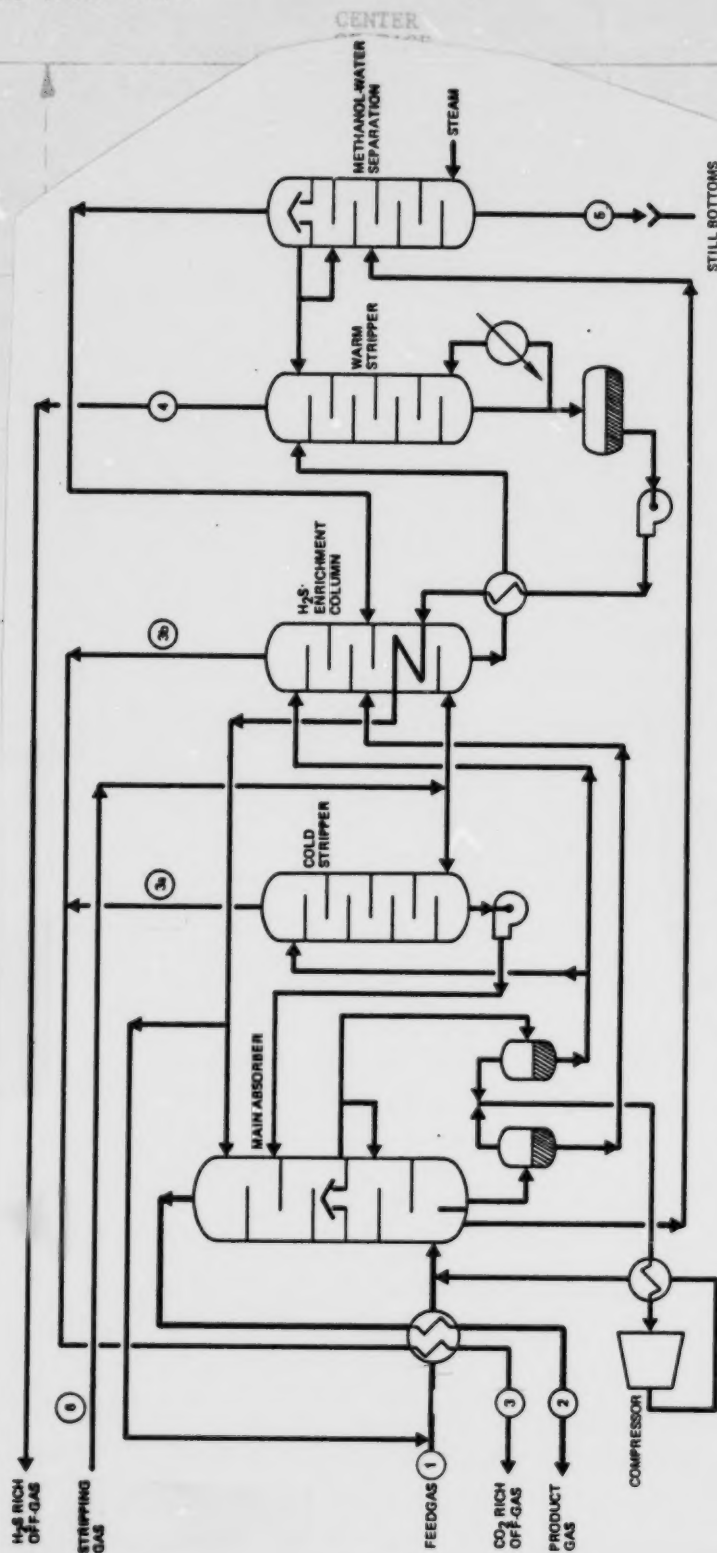


Figure 2-1. Simplified flow diagram of the Wilmington Rectisol unit (3,4)

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inert gas in the bottom section of the H_2S enrichment column. The stripping gas (Stream 6) is nitrogen, obtained at little additional cost from the oxygen plant which supplies oxygen to the partial oxidation generators. The bulk of the CO_2 is thereby stripped out, together with some H_2S which must be re-absorbed by means of a small stream of CO_2 -loaded methanol taken from the CO_2 absorber. The CO_2 -rich offgas (Stream 3b) from the top of the enrichment column is discharged to the atmosphere. The methanol solvent is cooled extensively in the H_2S enrichment column by flashing and stripping of CO_2 , thereby recovering much of the cold supplied to the wash tower in the form of refrigeration and sensible heat of the methanol. After warming the loaded methanol from the bottom of the H_2S -enrichment column against lean methanol, all the absorbed H_2S and CO_2 is stripped in the warm regeneration column with reboiled methanol vapor. The stripped gases (Stream 4) are sent to the Claus plant for sulfur recovery. The pure methanol is cooled and pumped back to the top of the wash tower for CO_2 absorption.

The main stream of CO_2 -loaded methanol leaving the CO_2 -absorption section of the wash column, after H_2 -recovery by flashing, is let down and stripped with nitrogen in the cold stripper to remove much of the dissolved CO_2 . The column overhead (Stream 3a) is discharged to the atmosphere. The cold, partly stripped methanol is returned to an intermediate tray of the CO_2 absorber. This subsidiary methanol circuit supplies additional cold to the wash tower and reduces the number of trays by increasing the solvent to gas ratio.

The methanol-water mixture condensed from the feed gas is separated in a still which produces pure methanol overhead and wastewater (Stream 5) in the sump. This keeps the water content of the circulating methanol at a low level.

Although methanol has a low vapor pressure at temperatures encountered in the Rectisol process, some is lost to the product and acid gas streams. The design solvent losses (vapor loss and a small allowance for leaks) are about 36 kg/hr and were achieved in actual operation.

In addition to the continuous process and waste streams, an intermittent process methanol blowdown stream is also taken at Wilmington. This purge controls the buildup of ammonia and associated increases in the refrigeration load, and also minimizes deposition of ammonium salts on heat exchange surfaces. The methanol purge stream is not indicated in Figure 2-1 due to its inter-

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mittent nature (purge frequency is on the order of once per month). It should be commented that this blowdown is not a standard operating feature of Rectisol units, but is simply an expedient measure to compensate for incomplete removal of entrained moisture and its dissolved ammonia in the final shift condenser before entering the Rectisol unit.

Published data on the characteristics of the Wilmington Rectisol gaseous process/waste streams are summarized in Table 2-1. Characterization data for the still bottoms from the methanol-water separation column and methanol purge have not been published. Data in Table 2-1 for the CO₂-rich offgas are presented as the combined CO₂-rich offgas (Stream 3); currently, however, characterization of CO₂-rich offgases must be obtained by sampling the cold stripper outlet (Stream 3a) and the H₂S enrichment column outlet (Stream 3b), and results must be composited.

TABLE 2-1. THEORETICAL GAS BALANCE FOR THE WILMINGTON RECTISOL UNIT (3,4)

Component	Stream Compositions, mole %				
	Feed Gas * (Stream 1)	Product Gas (Stream 2)	CO ₂ -rich Offgas(es) (Stream 3)	H ₂ S-rich Offgas (Stream 4)	Stripping Gas (Stream 6)
H ₂	62.35	94.08	0.31	--†	--
CO ₂	33.23	10ppmv	82.4	64.7	--
CO	3.24	4.86	0.08	--	--
N ₂	0.2	0.33	17.2	0.08	100
CH ₄	0.17	0.24	0.02	--	--
Ar	0.32	0.49	0.01	--	--
H ₂ S	0.49	<1ppmv	<5ppmv	35.2	--
COS	10ppmv	--	8ppmv	0.08	--
Flow (kmole/hr)	3992	2639	1567	55	269
Temperature, °C	43	36	30	30	30
Pressure, MPa	3.3	3.1	0.1	0.4	0.2

*Dry basis; moisture in feed gas (about 10 kmole/hr) exits the system as methanol/water still bottoms.

†Minor constituent for which data were not available.

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SECTION 3

TEST DESCRIPTION

In April of 1982 a pretest survey was conducted to determine the availability of sampling ports or lines. All existing sampling ports at the Rectisol unit were found to be suitable for sample acquisition, although minor modifications were required. These modifications were limited to providing short runs of piping to complete sample recirculation lines and/or vent lines and associated valving. Gas sampling ports are located in pressurized gas recycle loops through which a slip stream of the process gas may be passed. The recycle configurations and valving are such that all samples could be taken at ground level, in open air (an important safety concern). Samples of the still bottoms were also available from a ground level tap. Sample loop configurations did not permit the use of probes for flow rate measurements, and all flow rate temperature and pressure data were provided by Texaco from existing in-line equipment. Modification of the sample loops and recalibration of in-line flow measurement equipment were performed by Texaco during a scheduled plant downtime for maintenance in May.

In most cases, sampling lines were several meters in length. This was of some concern relative to obtaining representative samples, particularly of the Rectisol feed gas which contains both moisture and water-soluble species (e.g., NH_3). Also, the CO_2 -rich gas sampling lines were found to contain traces of solvent methanol at the start of the test, and it is uncertain whether all of this methanol was completely purged from the lines prior to the actual test period. The possible biases due to the loss of water-soluble species from the feed gas and of methanol contamination are addressed in Section 4.

The test period was from June 6 through 17, 1982. The shift and Rectisol units had been operating continuously for over a week after the May downtime so that steady operation existed at the start of the test.

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Except for a process upset June 12 and 13, the system operated under nearly the same conditions during the course of the test. The upset involved carry-over of shift condensate into the Rectisol unit and necessitated blowdown of a portion of the process methanol due to NH_3 buildup. Although no samples were taken for EPA on June 12 or 13, test data obtained subsequently did not indicate any influence of the upset on the subsequent performance of the Rectisol unit. Samples of process methanol taken by Texaco and Linde during the tests indicated that higher than design levels of water were present in the solvent. Although this water had some adverse effects on process performance, it had little impact on the characteristics of waste streams from an environmental standpoint.

The gaseous process/waste stream samples acquired during the test period and analyses performed are identified in Tables 3-1 and 3-2. With respect to the methanol still bottoms, the sampling schedule and analyses performed are summarized in Table 3-3. Where possible, standard sampling/analytical techniques were employed and the details of the procedures are presented in Sections 8 and 9. The first three days were dedicated to equipment setup, preliminary sampling and characterization to obtain order-of-magnitude stream compositions, and evaluation of the adequacy of proposed sampling and analytical methodologies. In addition, sample stability, storage requirements, and analysis time demand were determined. Material balance data were obtained during the last five days of testing.

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TABLE 3-1. SUMMARY OF GAS SAMPLES OBTAINED DURING THE RECTISOL TEST PROGRAM

Constituent	Sample Type	Streams Sampled*									
		Test Day 1 June 7	Test Day 2 June 8	Test Day 3 June 9	Test Day 4 June 10	Test Day 5 June 11	Test Day 6 June 14	Test Day 7 June 15	Test Day 8 June 16		
CO, CO ₂ , H ₂ , N ₂ , O ₂	Bomb†		1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4		
C ₁ -C ₆	Bomb†		1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4		
Aromatics	Bomb†										
Methanol	Bomb†			1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4		
H ₂ S, COS	Bomb†			1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4		
H ₂ S	Bottle‡						4	4	1		
SO ₂ , CS ₂ , Mercaptans	Bomb†			1			1		1,2,3a,3b,4		
NH ₃	Bomb/Train†		1,2,3a,3b,4		1,2,3a,3b,4		3a,3b,4	1	3a,3b,4		
HCN	Bomb/Train†		1,3a,3b		1,2,3a,3b		3a,3b	1	3a,3b		
HCN	Bomb†		1,2,3a,3b,4	1,2,4	3a,3b,4	4	1,2,3a,3b,4	1,2,3a,3b,4	1,2,3a,3b,4		
HCl, HF, HCOOH	Bomb/Train		1,2,3a,3b,4								
C ₆ hydrocarbons, S _n , Volatile trace elements (Hg,As,Se)	Train			1		3a,3b			3a,3b		

*Stream 1 - Rectisol feed gas; Stream 2 - Rectisol product gas; Stream 3a - CO₂-rich cold stripper offgas; Stream 3b - CO₂-rich enrichment column offgas; Stream 4 - H₂S-rich offgas.

†A single 0.5L Teflon lined sample bomb contains sufficient sample for analysis of all indicated species.

‡Pressurized composite bomb samples (11L aluminum bombs) of Streams 1 and 2 were returned to TMI for laboratory recovery in an NH₃/HCN absorption train or in an HCl, HF, HCOOH absorption train. On-site trains were employed for all other streams.

§Grab sample for wet analyses.

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TABLE 3-2. SUMMARY OF ANALYTICAL METHODS FOR GASEOUS CONSTITUENTS

Constituents	Sample Type	Principle of Analysis Method	Reference to Method
CO ₂ , CO, H ₂ , N ₂ , O ₂	Bomb	Gas chromatography/thermal conductivity detection	See Section 9
C ₁ -C ₆ hydrocarbons	Bomb	Gas chromatography/flame ionization detection	See Section 9
Aromatic hydrocarbons	Bomb	Gas chromatography/flame ionization detection	See Section 9
Methanol	Bomb	Gas chromatography/flame ionization detection	See Section 9
H ₂ S, COS, SO ₂ , mercaptans	Bomb	Gas chromatography/flame ionization detection	EPA Method 15 (Ref. 5)
H ₂ S	Glass bottle/ solution	Iodometric determination of sulfide in solution from acidification of CdS precipitate	Modified from EPA Methods 11 and 7 (Refs. 6,7)
NH ₃	Impinger solution	Basification of HCl impinger solution; distillation and Nessler finish	Welcher, F.J. (Ref. 8) plus APHA* 417B or D (Ref. 9)
HCN	Impinger solution	Basification of H ₂ SO ₄ impinger solution; distillation and Nessler finish	Welcher, F.J. (Ref. 8) plus APHA* 417B or D (Ref. 9)
HCN	Bomb	Gas chromatography/Hall detection	
HCl, HF, HCOOH	Impinger solution	Direct injection of carbonate impinger solutions into ion chromatograph	DIONEX applied notes (Refs. 10,11) plus Refs. 9 and 12
High molecular weight organics and elemental sulfur	XAD resin	Solvent desorption from resin; GC/MS identifica- tion and quantification	EPA (Refs. 13,14,15)
Volatile trace elements	Impinger solution	AAS-HGA analysis of H ₂ O ₂ and HNO ₃ impinger solutions	EPA (Refs. 13,14)

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TABLE 3-3. METHANOL STILL BOTTOMS SAMPLES/ANALYSES OBTAINED DURING THE RECTISOL TEST PROGRAM

Constituent/ Parameters	Preservation	Sample Description	Test Days Analyses Performed								Reference to Method
			1	2	3	4	5	6	7	8	
COD	None	1 liter	X	X	X	X	X	X	X	X	APHA* 508A (Ref 9)
SCN ⁻	--	From COD sample	X	X	X	X					APHA 412K (Ref 9)
pH and acidity	--	From COD sample	X								APHA 423 (Ref 9)
S ⁼	Zn acetate/ NaOH	500 mL	X	X	X	X					APHA 427B or D (Ref 9)
NH ₄ ⁺	H ₂ SO ₄	grab-100mL composite-1 liter	X	X	X	X					APHA 417 B or D (Ref 9)
CN ⁻	NaOH	1 liter	X	X	X	X					APHA 412 B or C (Ref 9)
TOC	Ice	1 liter	X	X	X	X	X	X	X		APHA 505 (Ref 9)
HCOOH	--	From TOC sample	X				X	X	X		Ref 16
Cl ⁻	None	1 liter	X				X	X	X		DIONEX applied notes #11 (Refs 11,12)
F ⁻	--	From Cl ⁻ sample	X				X	X	X		DIONEX applied notes #11 (Refs 11,12)
TDS	--	From Cl ⁻ sample					X	X	X		APHA 208A (Ref 9)
Phenols	Ice/H ₃ PO ₄ / CuSO ₄	1 liter	X	X	X	X	X	X	X		APHA 510A (Ref 9)
Extractable Organics	Ice	5 liters					X				EPA (Refs 13,14)
Oil & Grease	Ice, H ₂ SO ₄	1 liters							X		APHA 503C (Ref 9)

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SECTION 4

CONCLUSIONS AND EXTRAPOLATION OF TEST RESULTS

The Wilmington source test effort consisted of three principal phases: (1) development and evaluation of appropriate sampling and analysis methods; (2) data acquisition, reduction, and interpretation; and (3) extrapolation of the Rectisol environmental and performance data from an oil-fired POX application to coal gasification applications. This section summarizes the conclusions derived from the application of sampling and analysis methods developed for and/or validated during this test and conclusions resulting from data reduction and interpretation. Also, some of the factors which influence the design of Rectisol acid gas removal units are identified, and how these factors relate to extrapolation of the test data to coal gasification applications is discussed.

4.1 TEST DATA SUMMARY AND CONCLUSIONS

The Wilmington program resulted in the collection of both process and environmental data. These data are briefly summarized in this section and discussed from the standpoint of material balance closure, overall process performance, and characteristics of waste streams.

- Although operation of the HGU remained essentially constant during the test period, feed gas analyses indicate a change in the composition over time. Early test days are typified by higher H_2 , CO , and H_2S concentrations and lower CO_2 concentrations as compared with later test days. These trends cannot be attributed to changes in shift conversion performance since during such changes H_2 and CO_2 concentrations would decrease with increasing CO concentration and increase with decreasing CO concentration. This fact and the measured change in feed gas sulfur content suggest that the POX feedstock composition may have been changing during the test period. Alternatively,

a nonsystematic bias in the fixed gas analytical data is possible. The exact explanation of the empirical results is not of major importance from the standpoint of environmental assessment, and hence, the question is left unresolved. With regard to the characterization of process performance, the most significant parameter to vary in the Rectisol feed gas was the H_2S concentration which decreased from 3700 ppmv to 1400 ppmv during the test period. As a result, roughly proportional reductions of H_2S concentration in the H_2S -rich offgas were observed.

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- Measured and estimated flow rate data for the Rectisol process/waste streams were substantiated by material/species balance estimates for test days 4 through 8. Hydrogen and CO_2 balances were forced in order to obtain flow rate estimates for the product gas and enrichment column offgas streams, the only two gas streams for which flow rate measurements were not available. Flow rate estimates for these streams were substantiated by CO and N_2 closures within $\pm 6\%$. One standard deviation for closure based upon propagation of analytical uncertainty was estimated to be about 11%. Material closure for H_2S was typically within about two standard deviations of 100% (a standard deviation of about 15% was estimated based upon propagation of analytical uncertainties). Similarly, material closure for $Ar+O_2$ was typically within two standard deviations of 100% (an expected standard deviation of about 30% was estimated), although poorer closure was obtained during the early portion of the test period. Material closure for minor constituents such as COS and CH_4 were typically poorer than would be expected based upon analytical precision data, and in the case of COS there appears to be a bias toward low values for closure.
- The total CO_2 -rich offgas flow was comprised of about 12% cold stripper offgas and about 88% enrichment column offgas. The principal potential pollutant species in the CO_2 -rich offgases were H_2S , COS , CO , and methanol. Average concentrations of H_2S and COS in the combined CO_2 -rich offgas stream were 5.4 ppmv and 4.6 ppmv, respectively, resulting in an average total sulfur concentration of 10 ppmv. This

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concentration represents less than 0.4% of the total sulfur in the Rectisol feed gas. Varying H_2S concentrations in the Rectisol feed gas during the test period (i.e., from 0.37 to 0.14% H_2S) did not appear to influence the measured concentrations of H_2S in the CO_2 -rich offgas streams. It should be noted that COS balances indicate that between 24 and 44% of the feed gas COS is not accounted for in the CO_2 -rich offgases and the H_2S -rich offgas; thus, the COS content of either of these streams may be underestimated. Concentrations of CO in the combined CO_2 -rich offgas were about 700 to 800 ppmv, and corresponded to less than 3% of the CO in the Rectisol feed gas. Other inorganic species detected were NH_3 , HCN, and Cl which were present at concentrations of a few ppmv, or less, consistent with the low levels present in the Rectisol feed gas. Some portion of both NH_3 and Cl are believed to be attributable to entrained process methanol.

Methanol concentrations in the combined CO_2 -rich offgas were 490 to 880 ppmv. All other nonmethane organic compounds detected were present at concentrations below 1.6 ppmv each and contributed an additional 2.6 ppmv of total organics (primarily C_2 and C_3) to the combined CO_2 -rich offgas. All organic compounds detected in the CO_2 -rich offgases were also present in the Rectisol feed gas which indicates that no significant levels of other volatile organics enter the Rectisol unit with the makeup methanol or are generated within the process.

- H_2 was present at levels of over 1% by volume in the CO_2 -rich offgases for the latter part of the test period. This level is considerably higher than that for the plant design and may be related to off-specification operation of the recycle compressor (see Figure 2-1). H_2 loss in the CO_2 -rich offgases is primarily of process concern rather than environmental concern. No detectable levels of Hg, As, or Se were observed in the CO_2 -rich offgases. This is consistent with the absence of such elements in Rectisol feed gases and with

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limited historical information provided by Texaco on the composition of heavy oil feed to the POX unit.

- The principal constituents of environmental interest detected in the H_2S -rich offgas (or Claus feed gas) were H_2S , COS, and methanol. Over 99.8% of the H_2S and 60% of the COS in the Rectisol feed gas reported to the H_2S -rich offgas. Concentrations of 12 to 15% H_2S were measured during the last three days of testing which is much lower than the 35% levels which have been previously published. This difference is nearly proportional to the lower feed gas sulfur levels measured during this period as compared to published data. About 0.1% total organics were present in the H_2S -rich offgas, consisting almost entirely of methanol; ppmv concentrations of C_2 through C_6 hydrocarbons, benzene, and toluene were also detected.
- Still bottoms from the methanol/water separation column nominally contained 15% Rectisol condensate and 85% condensed steam from direct contact heating. Measured concentrations of $S^{=}$, CN^- , SCN^- , NH_4^+ , Cl^- , F^- , phenol, $HCOOH$, and oil and grease were typically a few mg/L, or less. TOC and COD levels were found to exceed levels attributable to CN^- , SCN^- , phenols, $HCOOH$, and oil and grease or $S^{=}$. Other organics, most probably methanol, are thus likely present in small amounts. Concentrations of most constituents would be expected to be higher if indirect heating were employed, although a corresponding decrease in still bottoms flow rate would result. The stream is very small in either case relative to other wastewater streams generated within the refinery and is likely to have little or no influence on subsequent wastewater treatment operations. In fact, reuse as process water makeup may be practiced if recycling of dissolved components is acceptable.
- Methanol losses in the product gas and offgas streams were estimated to be 0.009 to 0.013 kg/kmol of Rectisol feed gas as compared to published losses of about 0.0085 kg/kmol of feed gas (3). From 68 to 85% of the measured methanol loss was associated with the CO_2 -rich offgas

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streams. However, Texaco has indicated that heat exchangers originally provided in the Rectisol unit for methanol recovery from CO₂-rich offgases have been removed from service. In addition, some portion of the measured methanol levels may be due to entrainment/sample line contamination. In any case, the accuracy of estimated methanol losses cannot be verified since the acquisition of detailed methanol balance data was beyond the scope of this test program. The exact methanol losses in the Rectisol gas streams is primarily of process concern rather than environmental concern.

- Although NH₃, HCN, and HCOOH are known to be produced during gasification of heavy oils or water quenching of hot product gases, analyses of the Rectisol feed gas indicated that NH₃ and HCN were present at concentrations of less than 1 ppmv while formate was not found at a detection limit of about 0.05 ppmv. These analytical results are substantiated by the correspondingly low levels of NH₃, HCN, and HCOOH detected in gaseous and aqueous streams leaving the Rectisol unit. The low levels of NH₃, HCN, and HCOOH in the Rectisol feed gas are believed to be largely a consequence of treating shifted gas and of nearly complete moisture removal prior to acid gas removal. NH₃ is, to a large extent, absorbed in the shift condensate during the gas cooling which follows shift conversion. Major portions of the HCN and HCOOH produced during gasification or gas quenching are likely to be hydrolyzed during shift conversion, and most of any remaining load would be coabsorbed with the NH₃. Thus, while NH₃, HCN, and HCOOH are present in raw gases from heavy oil gasification, concentrations of these compounds are likely to be very low in the Rectisol feed gas when shift conversion precedes acid gas removal and when moisture is properly condensed from shift product gases.

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4.2 ADEQUACY OF SAMPLING AND ANALYTICAL TECHNIQUES

Prior to the Wilmington test, many of the analytical and sampling techniques envisioned for use had not been completely verified with matrices or target species levels which were to be encountered. In particular, the very

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high CO₂ levels in Rectisol gases and high H₂S levels in the Claus gas presented several potential problems. Also, it was expected that many of the species of interest would be present at sufficiently low levels where precision and accuracy could be affected by high blank levels, sample contamination problems, lack of analytical sensitivity, and/or low species collection efficiencies.

The subject test program provided the opportunity to validate certain methods for the levels of target species and matrices involved and to identify a number of limitations to EPA and/or other methods which have been used in other types of test programs. For sources involving fuel combustion, incineration, or sulfur recovery in refineries and coke plants, the gas matrices generally contain only a few percent of CO₂. In coal and oil gasification, most waste gases contain much higher levels of CO₂. Also, Rectisol gas streams constitute a much more reducing environment than do combustion gases so that collecting media designed for combustion sources are not necessarily applicable to Rectisol testing. The following are the major findings related to test methods. The findings should be generally relevant to testing of acid gas removal and sulfur control units in coal gasification facilities.

- H₂S and COS were readily quantifiable by the GC techniques employed at Wilmington in the range of 1 ppmv to about 1%. Higher H₂S levels present limitations of dilution with the use of flame photometric detectors. With thermal conductivity detectors, the detector response to H₂S is less precise than is the case with fixed gases such as CO₂, CO, or N₂. The relatively poor results obtained with thermal conductivity GC for high level H₂S samples (H₂S-rich offgas or Claus feed gas) are thought to relate to column saturation problems indicated by tailing peaks.
- H₂S can be readily quantified at percent levels using a wet chemical procedure adapted from EPA Methods 7 and 11. Grab gas samples are taken in evacuated glass bottles of known volume containing a CdSO₄ solution. The precipitated CdS is subsequently filtered, redissolved in acid, and the sulfide determined iodometrically. The method proved to be quite reproducible at Wilmington when compared to thermal conductivity GC data for H₂S at percent levels. Good H₂S material

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closure around the Rectisol unit was obtained when these grab sample data were used, suggesting that the method has no obvious bias.

- Standard GC techniques with flame ionization detectors are not sufficiently sensitive for precise quantitation of the very low levels of nonmethane aliphatics and aromatics in the subject gas streams. However, no problems of species separation were encountered, and no matrix effects could be identified.
- The presence of high levels of CO_2 in gases presents limitations with the use of alkaline impinger solutions for collection of HCN, since CO_2 tends to neutralize the solutions with consequent loss of HCN collection efficiency. Further, absorbed CO_2 can bias the measured sample gas volume. Only small sample volumes can be taken with gases containing more than a few percent of CO_2 , and correction must be made for absorbed CO_2 in the volume measurement. An alternative collection technique using 18M H_2SO_4 was verified prior to the Wilmington test and utilized in the field. In this technique, HCN is hydrolyzed by H_2SO_4 to NH_3 and CO with subsequent quantitation of the NH_3 formed. An NH_3 impinger must precede 18M H_2SO_4 for HCN collection, since any NH_3 in the gas would be collected along with HCN in the H_2SO_4 and subsequently measured as NH_3 . The detection limit of this technique is ultimately limited by sample volume and by the NH_3 blank level in the sulfuric acid; in the subject test the detection limit was about 0.1-0.2 ppmv.
- When levels of H_2S exceed a few percent in the sample gas, the H_2SO_4 technique for HCN cannot be used unless high levels of HCN are also encountered. H_2S reacts with SO_2/SO_3 in the acid to form elemental sulfur which quickly plugs the impinger frits. With high HCN levels, only small sample volumes need be taken for sufficient HCN collection for subsequent analysis. In such cases the sulfur interference can be tolerated.
- HCN can be determined in bomb samples of gases with high H_2S contents by GC using a Hall detector. This technique was verified prior to the Wilmington test with a detection limit of about 1 ppmv. Unfor-

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tunately, field data did not absolutely confirm the pretest results since HCN levels were at or below GC detection limits in all Wilmington samples.

- Ammonia could be collected in acid impinger solutions from the high CO_2 gases at Wilmington. Blank levels in dilute HCl tend to be much lower than in dilute H_2SO_4 , and the detection limit with HCL is about 0.1 ppmv.
- Indirect evidence suggests that some, if not most, of the measured NH_3 levels were contributed by process methanol which entered the sampling trains. Such methanol may have simply been residual in the sampling lines or may have been continuously entrained in the Rectisol gas streams. At the very low ppmv levels of NH_3 and Cl found at Wilmington, it is not of major significance from an environmental standpoint to distinguish between gaseous and methanol-derived material. From the process performance standpoint, however, the distinction is more important since it relates to overall methanol losses with the gas streams and to buildup of undesirable components in the circulating solvent. Special care in purging of sampling lines is required to minimize residual solvent methanol contamination of gas samples.
- Na_2CO_3 solutions were used in impingers to collect HCOOH , HCl, and HF from gas streams. The efficiency of collection of these species is not known since their concentrations were very low. Absorption of some CO_2 with corresponding neutralization of the impinger solution is not believed to have as large an impact on collection efficiency as that observed with HCN, since these species are much stronger acids than is HCN. The carbonate buffer could maintain the pH above 7 for the sampling times employed in the Wilmington test (2-4 hours).
- The collection efficiency of the heavy element oxidative impinger train for high CO_2 streams at Wilmington is believed to be similar to that observed in sampling of combustion gases. In the case of the H_2S rich offgas, the high H_2S levels quickly exhaust the H_2O_2 in the first impinger. Thus, an alternative technique is required for collection of volatile heavy elements in streams containing high levels of reduced sulfur species.

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- XAD-2 resin trap samples were taken of Rectisol feed gas and CO₂ off-gases. The method is targeted at organics with boiling points exceeding about 100°C although lower boiling compounds can be collected with reasonable efficiency if gas sample volumes are kept low (e.g., <1 m³). In the subject test, large sample volumes (about 3 m³) were taken to improve detection for higher boiling organics. With such volumes, collection efficiency for benzene and C₄ to C₆ hydrocarbons may be only 30% or lower. The sacrifice of collection efficiency was justified since separate on-site GC analyses were also conducted for C₁ through C₆ aliphatics and C₆ through C₈ aromatics. Although the C₆ through C₈ aromatics were present near or below detection limits of 0.1 to 0.5 ppmv, the XAD data and on-site GC data are at least reasonably consistent for C₇ and C₈ aromatics. The on-site GC data for benzene in the cold stripper offgas (Stream 3a) showed higher values than the XAD data, suggesting a low XAD collection efficiency as was expected. These results indicate that both direct GC and XAD measurements are needed when C₄ to C₇ organics at ppmv levels are key target species in a test program.

4.3 DIFFERENCES BETWEEN WILMINGTON RECTISOL AND RECTISOL UNITS FOR ENTRAINED COAL GASIFICATION

Several basic features of the Wilmington Rectisol unit would be found in essentially all Rectisol units, regardless of the type of service. However, feed gases which differ greatly in composition from those at Wilmington will involve somewhat different designs. Also, the requirements for product gas purity and offgas pollutant loadings will impact Rectisol design. Since the results of the subject test cannot be utilized for other units without a consideration of design differences, some of the factors which influence Rectisol design and how they relate to test results are discussed in this section. In the discussion of other Rectisol applications, the emphasis is on how the data from or features of the Wilmington Rectisol relate to these applications.

The characteristics of Rectisol feed gases are determined by (1) the specific gasification process, (2) the gasifier feed characteristics, (3) the position of shift relative to sulfur removal, (4) the end use of the gas

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which influences the extent of shift required, and (5) the final washing or moisture removal step(s) preceding Rectisol. The following is a discussion of the impacts of each of these factors on Rectisol feed gas characteristics. Although the major focus is upon entrained coal gasification applications, some comments regarding other applications are also included. Two examples of Rectisol designs are then examined to illustrate the influence of feed gas characteristics, product specifications, and of environmental requirements on design.

4.3.1 Differences in Crude Gases Among Gasification Processes

Although all fossil fuel derived feeds to entrained gasification or partial oxidation (POX) units yield qualitatively similar crude gases, definite differences exist in compositions which relate to feed characteristics and to the specific gasification process. For a specific oil feed, POX processes (specifically Texaco and Shell processes) generate very similar gases when oxygen and steam inputs are comparable.

In comparison to partial oxidation of oil, coal gasification can generate feed gases with widely differing characteristics depending upon the type of gasification employed. Coal gasification processes vary with respect to operating temperature and pressure. High temperature, entrained flow gasification processes such as the Texaco and Koppers-Totzek (K-T) processes are designed to operate at temperatures above ash fusion temperatures of coal (between about 1100°C and 1600°C). In contrast, the dry ash Lurgi gasification process operates at gasifier temperatures ranging from 500°C at the top (gas outlet) of the reactor to 1200°C at the reactor bottom. There are a number of other processes which operate between these temperature ranges, for example the Westinghouse or Winkler processes. Although gasification processes differ with respect to operating pressure, differences in operating pressure have much less effect upon gas composition than do differences in operating temperatures.

The crude gas from Texaco or K-T coal gasification has a composition similar to feed gas generated by Texaco or Shell oil POX, with only minor differences in H_2/CO ratio but higher concentrations of CO_2 and trace components. Lurgi gas has a quite different composition. It normally contains

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up to 10% methane and 1-2% of heavier hydrocarbons from ethane up to naphtha and benzene. At the same time, organic sulfur compounds (e.g., mercaptans and thiophenes) and also phenols and organic acids are present. In regard to these heavier components, raw Lurgi gas more closely resembles coke oven gas.

Entrained flow gasification systems generate essentially no organic compounds other than methane and formic acid. Formation of the latter compound appears to occur primarily during hot gas quenching/dust removal with wash water. The reaction of CO with steam is favored by high steam and CO partial pressures. Higher formic acid levels are reported with Texaco POX units than with Shell POX units, and while formic acid is produced in Texaco coal gasification/quench systems, no formic acid has been found in K-T product gas or wash waters.

Sulfur in fossil fuels is largely converted to H_2S and COS in entrained gasification units. In addition to H_2S and COS, mercaptans and thiophenes are also formed from feed sulfur in Lurgi gasification. For some coals with highly alkaline ash, several percent of the feed sulfur may be retained with the ash (including slag or dust). Coal-derived gases from high temperature gasification processes have COS/ H_2S ratios similar to those in oil-derived gases, and only small differences are seen among gasification processes for a given feed. With low temperature gasification processes such as Lurgi, COS/ H_2S ratios are lower than those in oil-derived gases. Total sulfur contents of coal gases will usually be higher than those of oil gases for two reasons. First, for a specific process the total dry gas production rate is lower for coals than for oils on a weight input basis. Secondly, many coals, especially those attractive for gasification, have sulfur contents higher than heavy oils. Although sulfur content of coal-derived gases tends to be higher, the H_2S/CO_2 ratio of key importance for selective Rectisol design may not necessarily be higher than in the oil case. This is because the CO_2 content of coal gases, especially after shift, is higher than that in the case of oil.

At the high temperatures encountered in entrained flow gasification, the organic nitrogen in the feed converts mostly to elemental N_2 , and to a lesser extent, NH_3 and HCN. In contrast, Lurgi gasification results in conversion of about half of the feed coal nitrogen to NH_3 . Direct data for the K-T

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gasification and indirect data for Texaco and Shell partial oxidation indicate that in all cases a few hundred ppmv each of NH_3 and HCN may be expected in crude gases. Differences in net NH_3 or HCN production among entrained processes and feeds are not especially significant from the standpoint of Rectisol design since these species usually would require almost complete removal prior to sulfur removal.

4.3.2 Effects of Shift Conversion on Rectisol Feed Gas Characteristics

For production of hydrogen or ammonia, synthesis gas must be almost completely shifted. For methanol synthesis, the gas need be only partially shifted while for acetic anhydride synthesis little or even no shift may be required. When only partial shift is needed, part of the gas bypasses the shift conversion unit and may be recombined with the shifted gas prior to removal of acid gases. This arrangement allows for adjustment of the bypass fraction to variations in crude gas composition and/or shift performance.

With either coal or oil as feeds, Texaco gasification facilities usually feature sulfur tolerant (or sour) shift preceding acid gas removal. In contrast Shell POX and K-T coal gasification facilities commonly feature shift after sulfur removal with a separate CO_2 removal step following shift. The location of shift, and the extent of shift required for different end uses, dramatically affects the characteristics of gases which Rectisol must process.

Sour shift catalysts typically achieve about 90% CO conversion. Conversion occurs in stages, with interstage heat recovery. After final cooling and condensate separation, the shifted gas is typically below 50°C . In addition to promoting the water gas shift reaction, sour shift catalyst is also active for the hydrolysis of COS. Thus, equilibrium is approached with respect to H_2S , CO_2 , COS, CS_2 , and H_2O at each stage, resulting in a cool gas with only a few ppmv of COS and less than 0.1 ppmv CS_2 . At Wilmington the $\text{H}_2\text{S}/\text{COS}$ ratio in shifted gas is about 500, and a similar ratio would be expected for other facilities where all of the crude gas is shifted prior to acid gas removal.

Sour shift catalysts are believed to be active for hydrolysis of HCN to form CO and NH_3 and for conversion of HCOOH to CO and H_2O . Thus, when all of the crude gas is shifted, very low levels of HCN and HCOOH would be

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expected after shift. The Wilmington data do show that less than 0.05 ppmv each of these species were present in Rectisol feed. From these data, however, it is not possible to determine whether HCOOH or HCN are destroyed during shift or absorbed in condensates after shift since no samples of shift feed gas or shift condensate were obtained.

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4.3.3 Effects of Gas Washing/Moisture Condensation on Rectisol Feed Gas Characteristics

Crude gases are always washed for entrained dust/ash removal. The major differences among processes are the temperatures at which the wash is conducted. In the case of Texaco oil or coal gasification, the hot gas leaving the reactor is quenched with water. In this manner dust is removed from the gas and at the same time the gas is saturated with water at a high temperature. After dust removal the gas can be fed directly to sour shift conversion without addition of steam. In the case of Shell POX and K-T coal gasification, the hot gas is first cooled in a waste heat boiler and then washed with cold water for dust and ash removal. Regardless of the specific process, considerable washing and moisture removal from the gas has taken place prior to Rectisol processing.

The washing/moisture condensation effects varying levels of removal of crude gas constituents. Ammonia is usually removed to a high degree due to its high water solubility. Formate, chloride, and fluoride are also highly water soluble as well as acidic, so that ammonia tends to enhance their removal. HCN is both less soluble in water than the above substances at 50°C and is such a weak acid that the presence of ammonia does not appreciably enhance its solubility. Hence, HCN can be present at ppm levels in washed gas unless it is destroyed over shift catalyst. Some of the H₂S present in crude gas may also be washed out, particularly if NH₃ levels are high, but the small amount of H₂S removed by this mechanism is not important from the standpoint of Rectisol design. The extent to which washing/condensation removes heavier elements is largely speculative, but on the basis of temperature reduction alone, some removal may be expected.

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The Wilmington data are not adequate to determine the extent of non-sulfur pollutant species removal from crude gas with moisture prior to Rectisol. Since shift feed gas and condensate samples were not taken, it

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is not clear whether condensation or destruction over shift catalyst is responsible for the low levels measured in the Rectisol feed gas. In the case of ammonia, there is indirect evidence that moisture removal is the major removal mechanism. During the test, an excursion occurred where moisture was carried over from the final stage cooler into the Rectisol unit. This resulted in a measurable NH_3 increase in the circulating methanol, necessitating a solvent purge to reduce the NH_3 loading. Clearly the entrained moisture contained ammonia.

With all coal gasification processes, crude gases contain entrained dust and volatile trace elements derived from the feed. The dust is mostly carbon in the case of oil gasification but contains larger amounts of inorganic ash in the case of coal. Generally, the dust component must be removed before acid gas removal, so that differences in dust loadings among coals and oils are not of major significance for Rectisol design. Volatile elements such as B, F, As, Se, Hg, and especially Cl are much more abundant in many coals than in heavy oils, and thus crude gases from coal would generally contain higher levels than would be found with oil.

4.3.4 Rectisol Acid Gas Removal in Coal Gasification Applications

Due to the different crude gas compositions which may be encountered, pretreatment and acid gas removal processes must be adapted on a case-specific basis. With only minor differences in prepurification steps, the crude gas from a Texaco or K-T gasifier can be processed in a Rectisol unit in a similar manner to that for an oil gasification crude gas. The process has only to be adapted to the different levels of CO_2 and H_2S in a totally or partially shifted gas which results in different flow rate and temperature profiles within the Rectisol system. In regard to offgases, nearly the same problems occur with either coal- or oil-derived gases.

Acid gas removal from a crude gas generated by a Lurgi coal gasifier is quite different. It is necessary to remove naphtha and the heavier components including phenol and mercaptans prior to H_2S and CO_2 removal in a pre-wash section with methanol. In case of a selective H_2S removal, the bulk of C_3 and C_4 hydrocarbons are removed together with the sulfur resulting in a H_2S fraction which may not be suitable for Claus processing without additional

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handling. The CO_2 fraction also contains a high loading of C_2 and C_3 hydrocarbons. In general, the handling of Lurgi generated crude gas results in a more complicated and more expensive process, although the general principles of physical wash processes (i.e., the application of Henry's law) can be used to design such units.

Since the design of the Wilmington Rectisol unit is most similar to designs suitable for treatment of gases from high temperature coal gasification, extrapolations of the data from oil gasification will be limited accordingly. Discussions in this section therefore relate to Rectisol acid gas removal in conjunction with Texaco and K-T gasification systems.

Texaco Coal Gasification/Single Stage Rectisol--

With Texaco coal gasification, the basic Rectisol design would be similar to that at Wilmington, and shift conversion would precede acid gas removal. With coal as a feed, higher levels of total sulfur in the Rectisol feed would be expected compared to those at Wilmington since most coals have higher sulfur levels than the vacuum oil feed at Wilmington and coal generates less total gas than oil on a weight input basis. Other than the total sulfur loading and concentration, the major differences between the Wilmington HGU and a coal gasification application relate to the extent of shift bypass rather than the gasifier feed. First, the CO_2 mass loading will be lower when only partial shift is required and the $\text{CO}_2/\text{H}_2\text{S}$ ratio would be lower. Second, COS levels would be higher when part of the gas bypasses shift. Third, CO levels are much higher with partial shift.

No Shift Bypass--

In this case the primary differences between a coal application and Wilmington are a potentially lower $\text{CO}_2/\text{H}_2\text{S}$ ratio and a higher ppmv level of COS. These differences translate into only minor changes in Rectisol design. The H_2S enrichment column would require more trays and/or additional wash methanol to separate COS from CO_2 in order to achieve a 10 ppmv residual in the CO_2 -rich offgas. A lower $\text{CO}_2/\text{H}_2\text{S}$ ratio would make it somewhat easier to obtain an enriched Claus gas compared to the Wilmington case.

Entrained moisture, NH_3 , and HCN should be kept to a minimum in Rectisol feed. There is no basis to expect levels of these constituents to be higher

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in Rectisol feed from coal after the entire volume of gas has been shifted and moisture properly condensed. The Wilmington data provide little insight into the question of volatile trace elements entering Rectisol, but in any case such elements would not be expected to be present in large enough amounts to influence Rectisol design or performance. Chlorine can be high in many coals, but that in the raw gas should be almost completely removed with condensate prior to Rectisol.

Shift Bypass--

When a portion of the crude gas bypasses shift, the combined shifted and unshifted gas to Rectisol will contain much higher levels of COS and CO than found at Wilmington. Also, the $\text{CO}_2/\text{H}_2\text{S}$ ratio will be much lower than found at Wilmington. The lower CO_2 loading would translate into a smaller CO_2 removal section of the main absorber. The higher COS level would, as noted previously, require more trays and/or wash solvent in the H_2S enrichment column. Although the relative volumes of the H_2S -rich and CO_2 -rich fractions may differ from those at Wilmington, design variations can still result in a CO_2 fraction containing less than 10 ppmv total sulfur and an H_2S fraction suitable as Claus feed.

At Wilmington the Rectisol feed gas contains about 2% CO and 60% H_2 . Although H_2 is only sparingly soluble in cold methanol, its high feed gas partial pressure results in about 2% removal in the main absorber. CO is somewhat more soluble than H_2 , but its lower partial pressure limits its removal. Absorbed H_2 and, to a lesser extent, CO are recovered by flashing the loaded methanol from the absorber to an intermediate pressure and recompressing the flash gas for recycle back to the feed gas.

The much higher levels of CO found in partial shift applications result in greater CO absorption and potential loss similar to that for H_2 at Wilmington. In addition to process CO loss considerations, the CO_2 -rich offgases may contain CO levels exceeding that permissible for direct discharge to the atmosphere. In such cases, it is possible to install two additional flash vessels for reduction of CO levels in CO_2 and H_2S loaded methanol after the flash vessel for H_2/CO recovery via recycle compressor. The new flash vessel for the H_2S loaded methanol must be equipped with some trays for H_2S removal,

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using a small part of the sulfur free solvent from the CO_2 removal section of the main absorber. By using two flash vessels in a selective Rectisol unit, a CO -rich flash gas is generated which can be recycled or incinerated. The CO content of the remaining CO_2 -rich tail gas can thereby be sufficiently low to enable direct venting to the atmosphere. The pressure of these additional vessels depends on the feed gas pressure, the CO and CO_2 content in the feed gas, and the CO emission limitations.

Shift bypass may result in levels of HCN after moisture condensation which are undesirable in Rectisol feed. As discussed previously, shift catalysts are believed to destroy HCN , and this may be the major reason for the low levels observed at Wilmington. If shift bypass results in higher levels of HCN in synthesis gas prior to Rectisol, two approaches to HCN removal have been used with Rectisol: a cold water wash or a methanol prewash. The water wash generates a cyanic wastewater for treatment consideration. The methanol HCN prewash would require a more complicated solvent regeneration step than in the case of H_2S regeneration and would require extra steam. Stripped HCN offgas from either water or methanol prewash could be routed to the Claus plant along with the H_2S -rich offgas. At the ppmv levels encountered in coal gasification, no problems are envisioned for Claus plants in handling the HCN , although it may be desirable to route HCN -rich offgases through the Claus burner. Alternatively, the stripped HCN offgas could be processed separately for HCN destruction by catalytic hydrolysis or thermal oxidation.

The Wilmington data indicate that NH_3 is ordinarily condensed with moisture to yield Rectisol feed gas containing only ppb levels. If entrained moisture is carried into the Rectisol unit, NH_3 tends to accumulate in the system. While this is not especially significant from an environmental standpoint, NH_3 buildup affects refrigeration load and hence operating costs and also can lead to salt deposition on heat exchange surfaces. Above a certain NH_3 level in the methanol, it is difficult to maintain column temperature profiles and thus stream purities. Consequently, heavy emphasis is placed upon removal of entrained moisture and NH_3 upstream of the Rectisol unit.

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Although formic acid is known to be present in crude Texaco gas, only traces were present in Rectisol feed at Wilmington. As in the case of HCN, it is unclear whether this reflects destruction during shift or condensation with moisture. If destruction over the shift catalyst is partially or largely the basis for the low measured values, then shift bypass would result in higher formate levels in synthesis gas to Rectisol. Formate is very water soluble, particularly in alkaline media, and thus removal with NH_3 -laden condensate might be expected. When coals with high Cl contents are gasified, shift condensates may be more neutral or even acidic, and in these cases some formate leakage into the Rectisol feed may occur.

With shift bypass, it is possible that small amounts of volatile heavier elements in coal derived crude gases may enter the Rectisol unit. Except for Cl, levels of such elements are not likely to be of concern from a process standpoint, although direct emissions to the atmosphere could occur via the CO_2 -rich gases or indirectly via the Claus tail gas. Trace amounts may also be found in the Rectisol condensate/still bottoms.

K-T Coal Gasification/Two Stage Rectisol--

In the Texaco based applications, direct water quenching yields a gas at high temperature, saturated with moisture which is suited to shift conversion prior to sulfur removal. If, however, the crude gas is indirectly cooled in a boiler or must be compressed before purification, it will contain only traces of moisture. In these cases, desulfurization prior to shift may be more economical. An alternate version of the Texaco gasification process, as well as the Shell partial oxidation (oil) process, and the K-T low pressure coal gasification process fall in this category. A major advantage of desulfurization before shift conversion is that the Rectisol feed gas contains much less CO_2 , which minimizes or even eliminates the enrichment step needed for generation of an H_2S -rich fraction suitable for Claus processing.

Two stage Rectisol differs from the Wilmington-type single stage design in that two separate absorption towers are used to first remove H_2S and COS and then to remove CO_2 following shift conversion. The first tower is analogous to the bottom portion of a Wilmington-type main absorber; the second tower similar to the upper portion. As at Wilmington, two nearly separate

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methanol circuits are maintained. The relative solvent rates to the sulfur absorption and to the CO_2 absorption circuits are similar between single and two stage designs since little CO_2 is actually absorbed in the sulfur removal section of either design.

Two-stage designs can achieve a selectivity which is at least as high as that achieved at Wilmington while maintaining similar residual sulfur levels in the CO_2 offgases. Test data for the Rectisol plant at Modderfontein, S.A. (a Linde designed, two-stage unit handling K-T gas) show that an H_2S -rich fraction suitable for Claus processing is obtained while generating a CO_2 offgas with less than 5 ppmv of H_2S (17). COS levels in feed gases to the H_2S absorber of a two-stage Rectisol will be much higher and CO_2 levels much lower than in single stage Rectisol since shift is downstream of sulfur removal. The higher concentrations of COS necessitate the use of additional trays and/or more wash methanol in the H_2S absorber and enrichment column to maintain low sulfur concentrations in the gas to shift and in the CO_2 -rich offgases.

Wilmington data relating to the relative flow rates of CO_2 offgas from the cold stripper and the enrichment column cannot be extrapolated to a two-stage Rectisol. At Wilmington the flow rate ratio of enrichment column offgas to cold stripper offgas is about 7, while at Modderfontein the ratio is less than 1. Also, the absolute and relative levels of COS and H_2S in the two gas streams may differ between one and two stage units. Only the combined CO_2 flow and total sulfur levels are similar.

Since sulfur removal precedes shift in two stage designs, the degree of shift needed for product gas end use does not impact sulfur removal or enrichment of the H_2S -rich fraction. In contrast, degree of shift has a direct impact for a single stage design. Locating shift conversion after sulfur removal results in a greater degree of CO absorption and loss compared to a single stage design since the feed gas contains much more CO. In addition, some CO will be removed in the second absorption stage, the amount depending on the extent of shift. Unless accounted for in design, these CO losses could result in unacceptable CO levels in the bulk CO_2 -rich offgases. The same approach discussed previously with single stage Rectisol designs would

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apply in this case: two or more flash stages of loaded methanol to recover H_2 and CO and generate a CO-rich flash gas which can be recycled or incinerated.

Since shift does not precede sulfur removal in two stage designs, no destruction or removal of HCN, HCOOH, or heavy elements is realized. Removal of such species must be accomplished by a water or methanol washing step upstream of Rectisol. The previous discussion regarding the shift bypass case with single stage Rectisol applied to two stage as well.

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SECTION 5

PRESENTATION OF THE DATA

This section presents the test data on a stream-by-stream basis without any detailed analysis or interpretation. However, discrepancies between results by different analytical methods and corrections necessitated by contamination of a few samples with air are discussed.

Six streams were sampled during the test period: Stream 1 - Rectisol feed gas, Stream 2 - product gas, Stream 3a - cold stripper offgas, Stream 3b - enrichment column offgas, Stream 4 - H_2S -rich offgas, and Stream 5 - methanol still bottoms. Although samples were collected for seven days of the eight day test program, data acquired through test day 4 are considered to be preliminary stream characterizations only. Thus, analyses performed during this period, particularly analyses for fixed gases, H_2S , NH_3 , and HCN are somewhat less accurate and/or less precise than analyses performed during the second half of the test period (test days 5 through 8). Analytical results for each stream are presented below.

5.1 RECTISOL FEED GAS (STREAM 1)

Analytical data for the Rectisol feed gas are presented in Table 5-1. Since shift conversion precedes acid gas removal, the major constituents in the feed gas are H_2 and CO_2 . Small amounts of CO , N_2 , Ar , H_2S , and COS are also present. Oxygen is not normally present but may be introduced into gas samples as a result of sample contamination with air. Argon and O_2 are indistinguishable by the specific gas chromatographic (GC) column employed and are therefore reported together. The relatively high N_2 and $Ar + O_2$ concentrations measured on test day 7 (2.21% and 0.64%, respectively) suggest sample contamination with air. It should be noted, however, that air contamination influences only the fixed gas analyses since they were performed on a common bomb sample, and that this level of contamination results

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TABLE 5-1. FEED GAS ANALYSES (STREAM 1)*

Constituent	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
H ₂ , vol %	GC	65.8	62.9	71	66.0	59.7	58.7		
CO, vol %	GC	3.16	2.95	1.78	2.88	1.49	1.53		
	-Orsat				1.7	1.7	1.8/1.5		
CO ₂ , vol %	GC	31.3	33.3	30.5	32.9	36.3	35.3		
	Orsat				32.5	35.3	35.2		
N ₂ , vol %	GC	0.56	0.34	0.32	0.26	0.17	2.21		
Ar + O ₂ , vol %	GC	0.16	0.08	0.10	0.08	0.07	0.64		
H ₂ S, vol %	GC	0.37	0.22			0.14	0.16		
	wet chem.						0.19		
CO ₂ , ppmv	GC		4	7		6	5		
CS ₂ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
SO ₂ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
RSH, ppmv	GC								
NH ₃ , ppmv	wet chem.	<0.2		0.1		0.1	<1.0		
HCN, ppmv	wet chem.	0.8		0.3		0.3			
	GC	<1	<1			<1	<1		
Cl, ppmv	wet chem.		3.6						
F, ppmv	wet chem.		<0.1						
Hg, ppbv	wet chem.		<0.01						
As, ppbv	wet chem.		<1.4						
Se, ppbv	wet chem.		<0.35						

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Constituent	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
C ₁ , ppmv	GC			600	570		590	645	
C ₂ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
C ₃ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
C ₄ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
C ₅ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
C ₆ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
Benzene, ppmv	GC								<0.5
Toluene, ppmv	GC								<0.5
Xylene, ppmv	GC								<0.5
Methanol, ppmv	GC								<0.5
HCOOH, ppmv	wet chem.			14	7		9	8	
Nonane, ppbv	GC/MS			<0.05					
Decane, ppbv	GC/MS			14					
Undecane, ppbv	GC/MS			17					
Benzene, ppbv	GC/MS			12					
Toluene, ppbv	GC/MS			20					
Xylenes, ppbv	GC/MS			453					
C ₃ - Benzenes, ppbv	GC/MS			490					
C ₄ - Benzenes, ppbv	GC/MS			120					
Sulfur (S ₈), ppbv	GC/MS			24					
C ₆ + sulfur, ppbv	GC/MS			2					
Naphthalene, ppbv	GC/MS			2					
Methyl Naphthalene, ppbv	GC/MS			11					
C ₂ -Naphthalene, ppbv	GC/MS			1.0					
Bis(2 ethylhexyl) phthalate, ppbv	GC/MS			0.5					
Phenol, ppbv	GC/MS			0.3					
Methyl Benzoic acid, ppbv	GC/MS			<0.1					
Methyl Phenols, ppbv	GC/MS			<0.1					
Dimethyl Phenols, ppbv	GC/MS			<0.1					
Total GC/MS compounds, ppbv				1178					
, ug/m ³				5100					
TCOF (100°C ≤ B.P. ≤ 300°C), ug/m ³				3000					
Grav ₃ (B.P. > 300°C) ug/m ³				160					

All analyses are presented on a dry gas basis. All less than values (e.g., <0.5 ppmv) indicate that the compound was not detected at this analytical detection limit.
Total chromatographable organics.

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in only about a 2% relative dilution of the corresponding H_2 , CO, and CO_2 levels. As a check on the GC analyses for CO_2 and CO, Orsat analyses of these constituents were also performed. Carbon dioxide analyses by both methods are in good agreement. Inconsistencies between CO analyses by GC and Orsat are primarily attributable to the low precision of Orsat analyses at low CO concentrations. A relative uncertainty of approximately 20% is estimated for an Orsat analysis of CO at a 2% concentration in the gas stream.

Although the feed gas moisture content was not directly measured, the gas is saturated and its temperature and pressure were measured. Typical temperatures and pressures during the test period were $42^{\circ}C$ and 2.9 MPa, respectively, corresponding to a moisture content of approximately 0.3%.

The only sulfur species detected in the feed gas were H_2S and COS. Concentrations of H_2S , the principal sulfur species, decreased during the test period from 0.37% to 0.14-0.19% which is substantially below the published H_2S concentration of 0.49% (see Table 2-1). Concentrations of COS ranged from 4 to 7 ppmv as compared with a published concentration of 10 ppmv. Carbon disulfide and SO_2 were not found at a detection limit of 0.5 ppmv and mercaptans (RSH) were not found at a detection limit of 1 ppmv. Other inorganic constituents detected in the feed gas were NH_3 , HCN, and Cl at ppm levels and elemental sulfur at ppb levels. The volatile elements F, Hg, As, and Se were not detected.

Methane was the principal organic compound detected in the feed gas, although ppm levels of methanol were also detected. Toluene and xylene, the principal aromatic compounds present, were detected at concentrations of about 0.5 ppmv by GC/MS. A variety of other aliphatic and aromatic compounds were also detected at ppbv levels. The total concentration of organics detected by GC/MS is $5100 \mu g/m^3$ which corresponds reasonably well with the TCO analysis ($100^{\circ}C \leq B.P. \leq 300^{\circ}C$) of $3000 \mu g/m^3$. The level of organics which are not detected by GC was $160 \mu g/m^3$ as determined by gravimetric analysis (Grav-organics have a B.P. greater than $300^{\circ}C$), or about 5% of the TCO plus gravimetric organics.

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Traces of aromatic hydrocarbons have previously been reported in product gases from Texaco coal gasification (18). Benzene was the most abundant

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aromatic compound; toluene and xylene levels were about one-tenth that of benzene. In contrast, the toluene and xylene levels at Wilmington exceed benzene by more than a factor of twenty. The source of toluene and xylene at Wilmington is believed to be naphtha used to separate soot from carbon scrubber wash water in the oil gasification section of the plant. Upon recycle, traces of naphtha in the wash water vaporize and are carried with raw product gases through shift and into the Rectisol unit.

5.2 PRODUCT GAS (STREAM 2)

Rectisol product gas analyses are presented in Table 5-2. The composition of the product gas is not of environmental significance although characterization data were obtained for material and species balance purposes. Product gas consisted primarily of H_2 with 2-3% CO . Carbon dioxide was generally present at concentrations below 200 ppmv while other fixed gases (e.g. N_2 and $Ar+O_2$) constituted approximately 0.6% of the product gas. Sulfur species, NH_3 , and HCN were not found at detection limits of 0.1 ppmv or less, as indicated. The only trace elements analyzed in this stream were Cl and F ; Cl was detected at less than 1 ppmv while F was not found at a 0.1 ppmv detection limit. The only organic compounds detected were CH_4 and methanol. Other organics were not found at detection limits below 0.5 ppmv, as indicated.

5.3 COLD STRIPPER OFFGAS (STREAM 3a)

Offgas from the cold CO_2 stripper comprised approximately 12% of the total CO_2 -rich offgases (H_2S enrichment column offgas accounted for the other 88%). Since CO_2 -rich offgases from the selective Rectisol process are typically vented directly to the atmosphere, characteristics of these gases are of interest from an environmental standpoint. As shown in Table 5-3, the cold stripper offgas consisted primarily of CO_2 and N_2 with less than 0.2% H_2 and less than 0.5% $Ar+O_2$. Carbon monoxide was not found with a detection limit of about 0.1%. The only sulfur species detected were H_2S and COS at total sulfur concentrations of less than 10 ppmv. Ammonia was detected at a concentration of 1 to 3 ppmv, and HCN was detected at 0.3 ppmv. Chloride was found at 2 ppmv while F , Hg , As , and Se were not found at detection limits below 0.1 ppmv.

TABLE 5-2. PRODUCT GAS ANALYSES (STREAM 2)*

Constituent	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
H ₂ , vol %	GC	>90	>90	97	98.0	98.0	95.6	94	
CO, vol %	GC	2.01	2.18	2.45	2.40	2.32	2.37	2.47	
	Orsat				2.3	2.2	2.2/2.3	2.3	
CO ₂ , vol %	GC	<0.1	0.34	<0.1	0.019	0.018	0.014	0.012	
	Orsat				<0.1	<0.1	<0.1	<0.1	
N ₂ , vol %	GC	0.37	0.46	0.62	0.47	0.38	0.45	0.38	
Ar+O ₂ , vol %	GC	0.1	0.06	0.16	0.16	0.12	0.17	0.14	
H ₂ S, ppmv	GC		<0.1	<0.1		<0.1	<0.1		
COS, ppmv	GC		<0.1	<0.1		<0.1	<0.1		
CS ₂ , ppmv	GC		<0.1	<0.1		<0.1	<0.1		
SO ₂ , ppmv	GC		<0.1	<0.1		<0.1	<0.1		
RSH, ppmv	GC								<0.1
NH ₃ , ppmv	wet chem			<0.1					
HCN, ppmv	wet chem			<0.1					
	GC	<1	<1			<1	<1	<0.5	
Cl, ppmv	wet chem		0.8						
F, ppmv	wet chem		<0.1						
C ₁ , ppmv	GC		820	880		740	1000		
C ₂ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₃ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₄ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₅ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₆ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
Benzene, ppmv	GC								<0.1
Toluene, ppmv	GC								<0.1
Xylene, ppmv	GC								<0.1
Methanol, ppmv	GC		140	170		130	72		
HCOOH, ppmv	Wet chem		<0.05						

* All less than values (e.g., <0.1 ppmv) indicate that the compound was not detected at this analytical detection limit.

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TABLE 5-3. COLD STRIPPER OFFGAS ANALYSES (STREAM 3a)*

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Constituent	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
H ₂ , vol %	GC	1.2	<0.1	<0.1	0.12	0.16	0.14	0.15	
CO, vol %	GC	<0.08	<0.1	<0.1	<0.1	<0.1	<0.1		
CO ₂ , vol %	GC	88.4	72.5	77.5	77.5	78.0	78.5	75.5	
	Orsat				81.0		79.4	80.0	
N ₂ , vol %	GC	8.0	23.8	19.1	18.5	19.5	18.0	18.7	
Ar+O ₂ , vol %	GC	0.42	1.36	0.40		0.34	0.07	0.45	
H ₂ S, ppmv	GC		2	5.1		6.9	6.1		
COS, ppmv	GC		1	4.3		2.4	2.0		
CS ₂ , ppmv	GC		<0.1	<0.1		<0.1	<0.1		
SO ₂ , ppmv	GC		<0.1	<0.1		<0.1	<0.1		
RSH, ppmv	GC					<0.1	<0.1		
NH ₃ , ppmv	wet chem	<0.2		3.4		1.0			<0.1
HCN, ppmv	wet chem	<0.2		<0.1		0.3			0.9
	GC	<1		<1		<1	<1		0.3
Cl ₂ , ppmv	wet chem		1.9						<0.5
F, ppmv	wet chem		<0.1						
Hg, ppbv	wet chem								
As, ppbv	wet chem				<0.012		<0.013		
Se, ppbv	wet chem				<0.11		<0.099		
C ₁ , ppmv	wet chem				<0.30		<0.37		
C ₁ , ppmv	GC		13	13		17	16		
C ₂ , ppmv	GC		10 [†]	10 [†]		2 [†]	10 [†]		
C ₃ , ppmv	GC		Trace [†]	Trace [†]		<0.5	Trace [†]		
C ₄ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₅ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₆ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
Benzene, ppmv	GC					<0.5	<0.5		
Toluene, ppmv	GC								Trace [†]
Xylene, ppmv	GC								Trace [†]
Methanol, ppmv	GC								<0.5
HCOOH, ppmv	GC		1900	1300		770	330		
	wet chem		<0.5						
Nonane, ppbv	GC/MS				12		12		
Decane, ppbv	GC/MS				3		15		
Undecane, ppbv	GC/MS				<0.1		<0.01		
Benzene, ppbv	GC/MS				5		9		

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Constituent	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
Toluene, ppbv	GC/MS					260		313	
Xylenes, ppbv	GC/MS					290		256	
C ₃ -benzenes, ppbv	GC/MS					22		22	
C ₄ -benzenes, ppbv	GC/MS					<0.1		0.1	
Sulfur (S ₈), ppbv	GC/MS					<0.1		<0.1	
C ₆ + sulfur, ppbv	GC/MS					<0.1		<0.1	
Naphthalene, ppbv	GC/MS					<0.1		<0.1	
Methyl Naphthalene, ppbv	GC/MS					<0.1		<0.1	
C ₂ -naphthalene, ppbv	GC/MS					<0.1		<0.1	
Bis(2 ethylhexyl) phthalate, ppbv	GC/MS					0.3		<0.1	
Phenol, ppbv	GC/MS					<0.1		<0.1	
Methyl benzoic acid, ppbv	GC/MS					<0.1		<0.1	
Methyl phenols, ppbv	GC/MS					<0.1		<0.1	
Dimethyl phenols, ppbv	GC/MS					<0.1		<0.1	
Total GC/MS Compounds, ppbv ₃						600		627	
, ug/m ³						2450		2580	
TCO (100°C ≤ B.P. ≤ 300°C), ug/m ³						2800		3100	
Grav ₃ (B.P. > 300°C), ug/m ³						30		30	

All less than values (e.g., <0.1 ppmv) indicate that the compound was not detected at this analytical detection limit.

*Trace indicates concentrations of approximately 0.5 to 1 ppmv.

*The GC peak positions for the C₂ analysis indicate ethylene or acetylene rather than ethane.

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The principal organic compound present in the cold stripper offgas was methanol at concentrations from 330 to 1900 ppmv. Methane and C₂ organics (ethylene or acetylene) were found at concentrations of 13 to 17 ppmv and 2 to 10 ppmv, respectively. Traces of C₃ organics were detected indicating concentrations of approximately 0.5 to 1 ppmv. Traces of benzene and toluene were also detected by GC. However, GC/MS analyses of the XAD-2 resin extracts indicate that benzene was present at concentrations of only 5 to 9 ppbv, and toluene and xylene were each present at concentrations of about 250 to 300 ppbv. The discrepancy between the on-site GC results and the off-site GC/MS results for benzene are thought to be the result of a combination of low collection efficiency by the XAD resin with the large sample volumes and losses due to volatility in sample preparation for GC/MS analysis. Toluene and xylene do not show discrepancies between the on- and off-site analyses as does benzene. Other organics detected at ppbv levels are nonane, decane, and C₃-benzenes. The total concentration of chromatographable organics detected by GC/MS was 2450 to 2580 µg/m³ which corresponds well with the TCO analyses of 2800 to 3100 µg/m³. The concentration of hydrocarbons too heavy to be detected by GC was 30 µg/m³ as determined by gravimetric analysis or about 1% of the TCO plus gravimetric organics.

5.4 H₂S ENRICHMENT COLUMN OFFGAS (STREAM 3b)

Offgas from the H₂S enrichment column comprised approximately 82% of the total CO₂-rich offgas from the test facility. As mentioned previously, the H₂S enrichment column offgas is an environmentally significant stream since it is typically vented directly to the atmosphere. Analyses of the enrichment column offgas presented in Table 5-4 indicate that the gas consisted primarily of CO₂ and N₂ with up to 1.7% H₂.

Measured concentrations of Ar+O₂ ranged from 0.07 to 4.27%. The values measured on test days 2, 6, and 7 are attributed to sample contamination with air. Since the fixed gas analyses (e.g. analyses for H₂, CO, CO₂, N₂, and Ar+O₂) are performed on a common gas sample, these analytical values require adjustment in the case of air contamination. Adjusted fixed gas concentrations estimated assuming an average Ar+O₂ concentration of 0.27% are presented in Table 5-5. The apparent air contamination corresponds to 12%

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TABLE 5-4. H₂S ENRICHMENT COLUMN OFFGAS ANALYSES (STREAM 3b)*

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Constituent	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
H ₂ , vol %	GC		1.3	<0.1	<0.1	1.56	0.95	1.70	1.65
CO, vol %	GC		0.08	0.08	<0.1	<0.1	<0.1	<0.1	
CO ₂ , vol %	GC		77.5	80.7	84.5	77.5	58.2	84	82.8
	Orsat					78.9		88/90	84.6
N ₂ , vol %	GC		16.2	15.1	13.5	13.1	25.3	15.3	12.6
Ar+O ₂ , vol %	GC		2.68 [†]	0.56	0.30	0.15	4.27 [†]	1.26 [†]	0.07
H ₂ S, ppmv	GC			5	6.7		3.6	6.5	
COS, ppmv	GC			5	5.1		4.5	5.2	
CS ₂ , ppmv	GC			<0.1	<0.1		<0.1	<0.1	
SO ₂ , ppmv	GC			<0.1	<0.1		<0.1	<0.1	
RSH, ppmv	GC								<0.1
NH ₃ , ppmv	wet chem		0.1		1.0		0.3		0.1
HCN, ppmv	wet chem		<0.2		<0.1		0.7		<0.1
	GC		<1		<1		<1	<1	<0.5
Cl, ppmv	wet chem			<0.1					
F, ppmv	wet chem			<0.1					
Hg, ppbv	wet chem					<0.013		<0.016	
As, ppbv	wet chem					<0.093		<0.13	
Se, ppbv	wet chem					<0.33		<0.37	
C ₁ , ppmv	GC			90	100		82	130	
C ₂ , ppmv	GC			Trace [‡]	Trace [‡]		Trace [‡]	Trace [‡]	
C ₃ , ppmv	GC			<0.5	Trace [‡]		Trace [‡]	Trace [‡]	
C ₄ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
C ₅ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
C ₆ , ppmv	GC			<0.5	<0.5		<0.5	<0.5	
Benzene, ppmv	GC							<1	
Toluene, ppmv	GC							<0.5	
Xylene, ppmv	GC							<0.5	
Methanol, ppmv	GC			740	700		450	800	
HCOOH, ppmv	wet chem			<0.05					
Nonane, ppbv	GC/MS					4		7	
Decane, ppbv	GC/MS					6		10	
Undecane, ppbv	GC/MS					<0.1		<0.1	
Benzene, ppbv	GC/MS					7		6	

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Constituents	Analysis Method	Test Day							
		1	2	3	4	5	6	7	8
Toluene, ppbv	GC/MS					267		240	
Xylenes, ppbv	GC/MS					215		232	
C ₃ -benzenes, ppbv	GC/MS					18		19	
C ₄ -benzenes, ppbv	GC/MS					<0.1		<0.1	
Sulfur (S ₈), ppbv	GC/MS					<0.1		<0.1	
C ₆ + sulfur, ppbv	GC/MS					<0.1		<0.1	
Naphthalene, ppbv	GC/MS					<0.1		<0.1	
Methyl Naphthalene, ppbv	GC/MS					<0.1		<0.1	
C ₂ -naphthalene, ppbv	GC/MS					<0.1		<0.1	
Bis (2 ethylhexyl) phthalate, ppbv	GC/MS					<0.1		0.3	
Phenol, ppbv	GC/MS					<0.1		<0.1	
Methyl benzoic acid, ppbv	GC/MS					<0.1		<0.1	
Methyl phenols, ppbv	GC/MS					<0.1		<0.1	
Dimethyl phenols, ppbv	GC/MS					<0.1		<0.1	
Total GC/MS Compounds, ppbv ₃ , $\mu\text{m}/\text{m}^3$						517		514	
TCO (100°C ≤ B.P. ≤ 300°C), $\mu\text{m}/\text{m}^3$						2100		2130	
Grav. (B.P. > 300°C), $\mu\text{g}/\text{m}^3$						2700		2800	
						<1		<1	

* All less than values (eg. <0.1 ppmv) indicate that the compound was not detected at this analytical detection limit.
 * The high Ar+O₂ values measured on test days 2, 6, and 7 are believed to result from contamination of the gas sample with air. Since the fixed gas analyses (eg. H₂, CO, CO₂, N₂, and Ar+O₂) were performed on a common gas sample, each of these analyses requires adjustment in the case of air contamination.
 * Trace indicates concentrations of approximately 0.5 to 1 ppmv; the C₂ hydrocarbon peak positions by GC analysis indicate either ethylene or acetylene rather than ethane.

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sample dilution on test day 2, 19% sample dilution on test day 6, and 5% sample dilution on test day 7.

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TABLE 5-5. ADJUSTED FIXED GAS GC ANALYSES FOR H₂S ENRICHMENT COLUMN OFFGAS (STREAM 3b)*

Constituent	Test Day	Adjusted Concentration, vol %		
		2	6	7
H ₂		1.5	1.2	1.79
CO		0.09	<0.1	<0.1
CO ₂		87.7	72.1	88
N ₂		7.92	12.5	12.1
Ar+O ₂		0.27	0.27	0.27
Total		97.5	86.1	102.2

* Measured fixed gas analyses have been adjusted for air contamination assuming an average Ar+O₂ concentration of 0.27% in the gas stream.

Other inorganic constituents present in the enrichment column offgas are CO at less than 0.1%, H₂S and COS at approximately 5 ppmv each, NH₃ at 0.1 to 1 ppmv, and HCN at less than 1 ppmv. Sulfur species such as CS₂, SO₂, and mercaptans were not detected, and trace elements such as Cl, F, Hg, As, and Se were not detected.

The principal organic compounds detected were methanol and methane at concentrations of 450 to 800 ppmv and 80 to 130 ppmv, respectively. Traces of C₂ and C₃ organics were detected at approximately 0.5 to 1 ppmv each. Toluene and xylene were present at levels of 200 to 300 ppbv while all other chromatographable organics were present at concentrations of less than 20 ppbv. The total concentration of organics according to GC/MS analysis was approximately 2100 µg/m³ which compares well with the TCO analysis of 2700 to 2800 µg/m³. No non-chromatographable organics (B.P. >300°C) were detected (less than 1 µg/m³).

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5.5 H₂S-RICH OFFGAS (STREAM 4)

Essentially all of the sulfur present in the Rectisol feed gas leaves the Rectisol unit with the H₂S-rich offgas. At the Wilmington refinery the H₂S-rich offgas is processed through the Claus sulfur plant. This stream is of environmental significance since its characteristics influence sulfur plant design and operation, and thus the overall emission of sulfur compounds. Analyses of the H₂S-rich offgas are presented in Table 5-6. The stream consisted primarily of CO₂ and H₂S, with measured H₂S concentrations ranging from 12 to 25% during this test period. However, GC analyses on test days 4 through 6 appear high based upon species balance considerations. This is attributed to the fact that GC analyses of concentrated H₂S streams are often associated with column saturation problems and tailing peaks. Therefore, wet chemical analyses were employed as a check of the GC values. Also, some technical improvements were made in the GC technique after test day 5. Both the wet chemical analyses and GC analyses on test days 7 and 8 are considered to be more accurate than the GC analyses performed on test days 4 through 6.

Nitrogen and Ar+O₂ analyses performed on test days 2 and 3 appear to indicate air contamination of the gas samples for fixed gas analyses on these two days. Data from test days 4 through 8 indicate total N₂ and Ar+O₂ concentrations of less than 2%. The other fixed gases, H₂ and CO, were not found at a detection limit of 0.1%.

Other inorganic constituents detected in the H₂S-rich offgas are COS, NH₃, and Cl. Concentrations of COS ranged from 140 to 190 ppmv. CS₂ and RSH were not detected. SO₂ could not be readily resolved from H₂S in the GC columns employed when H₂S was present at over a few percent. Ammonia was detected at concentrations below 1 ppmv, and Cl was detected at about 2 ppmv. Cyanide was not found in the offgas by GC analyses with a detection limit of approximately 1 ppmv. The more sensitive wet chemical analyses for HCN from impinger solutions could not be performed, as the high H₂S levels resulted in the formation of elemental sulfur in the sulfuric acid impingers which quickly caused clogging.

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TABLE 5-6. H₂S-RICH OFFGAS ANALYSES (STREAM 4)*

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Constituent	Method	Test Day							
		1	2	3	4	5	6	7	8
H ₂ , vol %	GC	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CO, vol %	GC	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CO ₂ , vol %	GC	54	81.7	81.0	79.8	82.5	80.8	80.7	80.7
N ₂ , vol %	GC	16.2	11.7	0.18	1.84	0.33	0.37	1.04	1.04
Ar+O ₂ , vol %	GC	5.11		0.12	0.1	0.06	0.05	0.18	0.18
H ₂ S, vol %	GC			25	24.4	21.1	12.0	15.2	15.2
	wet chem					13.3	12.7		
COS, ppmv	GC	140		190		160	150		
CS ₂ , ppmv	GC								<0.5
SO ₂ , ppmv	GC	+		+		+	+		
RSH, ppmv	GC								<0.1
NH ₃ , ppmv	wet chem	0.4		0.1		0.2			<0.1
HCN, ppmv	GC	<1	<1.2	<1.2	<1.2	<1.2	<1.2	<0.7	<0.7
Cl, ppmv	wet chem		1.9						
F, ppmv	wet chem		<0.1						
C ₁ , ppmv	GC		<0.5	<0.5		<0.5	<0.5		
C ₂ , ppmv	GC		7	6		4	8		
C ₃ , ppmv	GC		1	2		1	2		
C ₄ , ppmv	GC		3	4		2	5		
C ₅ , ppmv	GC		2	4		1	1		
C ₆ , ppmv	GC		2	5		2	3		
Benzene, ppmv	GC								Trace [†]
Toluene, ppmv	GC								Trace [†]
Xylene, ppmv	GC								<0.5
Methanol, ppmv	GC		910	840		880	1000		
HCOOH, ppmv	wet chem		<0.05						

* All less than values (e.g., <0.1 ppmv) indicate that the compound was not detected at this analytical detection limit.

[†]Trace indicates concentrations of approximately 0.5 ppmv for benzene and toluene.

*SO₂ could not be resolved from H₂S by the GC columns employed when very high H₂S levels were encountered.

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Organics detected in the H_2S -rich offgas included methanol, C_2 - C_6 hydrocarbons, benzene, and toluene. Methanol was the principal organic compound with concentrations of approximately 0.1%. Although methane was not detected, C_2 through C_6 hydrocarbons were generally present at concentrations of a few ppmv each. Traces of benzene and toluene were detected at approximately 0.5 ppmv each.

5.6 METHANOL STILL BOTTOMS (STREAM 5)

Moisture present in the Rectisol feed gas is ultimately removed from the process methanol by distillation. Direct contact steam heating is employed at Wilmington. 15% of the methanol still bottoms is Rectisol condensate while the remaining 85% is condensed steam. Analyses of the methanol still bottoms are presented in Table 5-7.

As indicated by the data, nonvolatile inorganic dissolved solids are relatively low (34 mg/L). S^{2-} , SCN^- , NH_3 , and Cl were detected at concentrations of a few mg/L. Cyanide and F were detected at concentrations ranging from 0.1 to 0.5 mg/L. Chloride was measured at approximately 5 mg/L on test day 3 but was not found on test days 6 and 7 at a detection limit of 0.1 mg/L.

Analyses were also performed for phenols, formate, and oil and grease indicating mg/L levels of each. With the exception of phenols, no chromatographable organics were found at a detection limit of 1 μ g/L. Total organic carbon (TOC) and chemical oxygen demand (COD) were generally below 33 mg/L and 118 mg/L, respectively. Analysis of a methylene chloride extract of one still bottoms sample by GC/MS indicated about 0.4 mg/L of phenolic compounds. No other organics were detected in the extract.

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TABLE 5-7. METHANOL STILL BOTTOMS ANALYSES (STREAM 5)*

Constituent	Test Day	Concentration, mg/L (except for pH)							
		1	2	3	4	5	6	7	8
pH			6.2						
S ⁼	<2	1.2	1.2	1.3					
CN ⁻ (as HCN)		<0.5	0.45	0.15					
SCN ⁻	2.7	2.1	3.0	2.4					
NH ₄ ⁺ (as NH ₃)	2.4	2.0	2.5	4.3					
Cl ⁻			4.7				<0.1	<0.1	
F ⁻			0.1				0.4	<0.1	
Phenols			2.7	1.5	0.8 [†]	1.8	1.6	0.5	
HCOOH			0.9				0.7	0.6	
Oil and grease							6.1	0.8	
TDS						34	17	8	
TOC			33	9	8	7		6	
COD	39	22	118	25	14	28		90	
Acidity as CaCO ₃		<4							

* Still bottom samples nominally consist of 15% Rectisol condensate and 85% condensed stripping steam since direct steam heating is employed.

† Analysis of a separate sample on test day 5 by GC/MS indicated 64 µg/L phenol, 210 µg/L methyl phenols, and 96 µg/L dimethyl phenol. No other chromatographable organics were found at a detection limit of 1 µg/L.

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SECTION 6

PRECISION AND ACCURACY OF THE DATA

The primary purpose of the subject test program was to generate data relating to the species/parameters of environmental interest. In addition, data were collected which relate primarily to the overall performance of the Rectisol unit from the process standpoint. Analytical techniques were selected with major focus on their accuracy and precision for key species of environmental interest.² In the case of species primarily of process concern, some of the techniques employed were less accurate or precise than would be desired for a detailed engineering evaluation of process research studies (e.g., for close material balance closure). In order to properly interpret the results of the test program, it is necessary to have estimates of the precision (or repeatability) and accuracy (or bias) of the sampling and analytical methods employed. These estimates can assist in (1) determining the detection limits of the specific methods, (2) identifying spurious samples or analyses, (3) assessing whether differences in stream characteristics are statistically significant or simply reflect analytical scatter, and (4) in determining the uncertainty expected in material balance closure due to propagation of sampling and analytical errors.

Precision is usually expressed as the variance or its square root, the standard deviation of a replicate data set. Since there may be several sources of variance in a set of replicate data, the precision estimate reflects the relative contributions of such sources. Generally, a distinction is made between analytical variance and sample variance. The former refers to the repeatability or precision of the analytical technique given constant sample characteristics. The latter refers to the overall variance observed when replicate samples are taken and carried through the analytical procedure. In some cases the relative contributions of analytical and sample variances are not readily determined.

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The accuracy of data is often more difficult to assess than precision. For certain types of analyses such as NH_4^+ or CN^- in aqueous media, the spike recovery approach is employed. For other types, such as GC analysis of gases, spiking can itself introduce large errors. In such cases, analysis of standards or samples by other methods can provide an indication of any systematic bias.

Prior to the subject test, only limited precision and accuracy data were available for many of the methods employed. To provide a data base for these methods, over 10% of the samples/analyses in the subject test were replicated. Also, after initial analyses, selected samples were spiked with known amounts of specific constituents for subsequent analysis. In this section the replicate and spike data are summarized by type of analysis or constituent. Precision data are reported as absolute and relative sample standard deviations (RSD) which have been calculated by geometrically averaging the standard deviations of pairs or sets of replicates. Spike recoveries are reported as averages of percent recoveries. Also, the number of replicates and spikes along with the total number of determinations are indicated for most types of analyses.

6.1 GASEOUS SULFUR SPECIES BY GC/FPD

Replicate GC/FPD injections were conducted for H_2S and COS with about half of the "onsite" gas samples taken at Wilmington. Table 6-1 summarizes the results of these replicates. The H_2S concentrations in the various streams sampled varied greatly, therefore the relative standard deviation (RSD) for these measurements was calculated at two H_2S levels. The higher RSD for the low level of H_2S is consistent with observations during the method verification phase of this test program. No replicate analyses for CS_2 , SO_2 , or mercaptans were performed since these species were not found above 0.5 ppmv in any gas sample at Wilmington.

Two gas standards (supplied by Scott Environmental, Inc.) were used during this study. The concentrations of the various species in these standards (certified by Scott) are given in Table 6-2. The accuracy of the sulfur species standard 1 is $\pm 5\%$ relative, of standard 2 is $\pm 1\%$ relative. These values are interpreted as bias limits where data for sulfur species by different methods or by GC using other standards are compared.

TABLE 6-1. SUMMARY OF REPLICATE INJECTION RESULTS FOR SULFUR COMPOUNDS BY GC/FPD

Compound	Concentration Range	Number of Replicate	Total Analyses	Avg. RSD*
H ₂ S	1-10 ppmv	13	21	11%
H ₂ S	1400-4000 ppmv	8	13	4%
COS	1-200 ppmv	15	24	5%

*Geometric mean, Relative Standard Deviation

TABLE 6-2. CONCENTRATION OF SULFUR GC STANDARDS IN PPMV

	Standard #1* (Cal 6967)	Standard #2† (AAL 8111)
H ₂ S	36	4970
COS	36	49.8
CS ₂	36	49.8
CH ₃ SH	39	9.97
C ₂ H ₅ SH	35	9.94

*In N₂, ±5% relative

†In N₂, ±1% relative

Injection volumes were adjusted to produce a range of concentrations for calibration. Sample volumes were also adjusted to fall within the linear range of the calibrated detector.

6.2 GASEOUS HYDROCARBON SPECIES ANALYZED BY GC/FID

Replicate GC/FID injections were performed on over 15% of the samples analyzed for C₁-C₆ hydrocarbons and methanol (Table 6-3). In all cases 1 mL of sample was injected for analysis since C₁-C₆ organics were only in the low ppmv range (while methanol concentrations were much higher).

TABLE 6-3. SUMMARY OF REPLICATE INJECTION RESULTS FOR COMPOUNDS DETERMINED BY GC/FID

Compound	Concentration Range (ppmv)	Number Replicates	Total No. Analyses	Avg. RSD**
Methanol	2 - 1500	4	24	1%
Methane	ND - 1000	4	22	3%
C ₂ (as ethane)	ND - 10	4	22	4%
C ₃ (as propane)	ND - 2	4	22	12%
C ₄ (as butane)	ND - 5	4	22	10%
C ₅ (as pentane)	ND - 4	4	22	13%
C ₆ (as hexane)	ND - 5	4	22	11%

ND = not detected (detection limit -0.1 ppmv)

*Geometric mean of Relative Standard Deviations

Injection volumes for the gas standards were adjusted to provide a calibration range which was linear over a very wide range ($>10^4$). Detection limits of about 0.1 ppmv are estimated for the subject organics. For this reason no problems were anticipated for these analyses other than interferences. The actual chromatographs of the gas samples taken at Wilmington proved to be very "clean" for the target species and no problems with range were encountered.

The C₁-C₆ hydrocarbons were standardized using gas standards supplied by Scott Environmental Inc. as given in Table 6-4. Methanol standards were prepared in liquid form in methylene chloride for calibration purposes and microliter amounts were injected on column.

6.3 FIXED GAS ANALYSES BY GC/TC

The precision of the fixed gas replicate injections are shown in Table 6-5. Approximately half of the analyses were replicated since these components constituted the major portion of the gas samples analyzed. As can be seen in Table 6-5, the precision of the measurements are inversely proportional to observed concentration. This result is consistent with pretest

TABLE 6-4. HYDROCARBON GC STANDARDS

	Standard 1* (ppmv)	Standard 2† (ppmv)
Methane	96.6	14.9
Ethane	106	14.5
Propane	98.5	15.5
Butane	97.9	15.2
Pentane	89.5	16.1
Hexane	97.5	15.7

* In N₂, ±2% relative accuracy or bias

† In N₂, ±10% relative accuracy or bias

observations. Standards for the fixed gases were supplied by Scott Environmental Inc., and injection volumes were adjusted for both standards and samples to remain within the calibrated range of the detection. O₂, N₂, and CO standards are indicated by Scott to be ±2% relative accuracy. Pure CO₂ and H₂ compressed gases were used as standards for those species, each with over 99.9% purity.

TABLE 6-5. SUMMARY OF REPLICATE INJECTION RESULTS FOR COMPOUNDS DETERMINED BY GC/TC

Compound	Concentration Range (%v)	Number Replicates	Total No. Analyses	Avg RSD*
O ₂	0.1 - 3	23	49	12%
N ₂	0.2 - 25	24	49	8%
CO	0.1 - 3	19	50	8%
CO ₂	35 - 85	27	53	1%
H ₂	60 - 100	16	46	1%

*Geometric mean

6.4 CO AND CO₂ ANALYSES BY ORSAT

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Table 6-6 presents the results of duplicate Orsat analyses for CO and CO₂. At the 35% CO₂ level, the relative standard deviation is less than 0.6%, while in the 75-90% CO₂ range up to 2% is seen. At the 1.5 to 2.5% CO level found in Streams 1 and 2, the Orsat method shows a rather poor precision with a relative standard deviation of up to 24%. Precision of Orsat analyses tend to be highly dependent on the skill of the operator.

6.5 IMPINGER SAMPLES

HCN, NH₃, HCOOH, Cl, F, Hg, As, and Se in the gas phase were determined by analysis of impinger solutions. The analytical precision data is summarized in Table 6-7. For NH₃ and HCN (measured as NH₃), relative standard deviations are 1.6 to 2.5%. For Cl, F, and Hg the relative standard deviations are much higher, reflecting the very low levels of these constituents in the samples. For formate, As, and Se, all samples were below detection limits so that no analytical precision estimate could be made.

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Several duplicate trains were run at Wilmington for NH₃ and HCN, and these results are shown in Table 6-8. The sample precision based on these data is about 7-16% for NH₃. The only replicate samples which were above the detection limit for HCN gave identical values (two significant figures), and hence the minimum possible sampling precision is taken as the analytical precision of 2%. For purpose of subsequent analysis, the sampling and analytical replicate data were pooled to obtain geometric mean relative standard deviations of 6.5% for NH₃ and 2.0% for HCN.

It might be expected that HCN would be less precise than NH₃ since NH₃ levels in the gases sampled are higher than HCN levels. Both species are ultimately measured as NH₃. Both the 0.1M HCl and 18M H₂SO₄ used in the impingers contain NH₃ which must be subtracted from the sample values as blanks. The HCl contains the equivalent of about 0.1 to 0.3 ppmv of NH₃ in the gas for the sample volumes of 300 to 100 L. The H₂SO₄ contains ammonia equivalent to about 3 ppmv of gaseous HCN for the above samples. Thus, the absolute NH₃ levels of total blank-plus-sample were much higher in the case of HCN than in the case of NH₃. With the analytical technique used, this results in a greater sensitivity or precision for replicate analyses of sulfuric acid impingers.

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TABLE 6-6. SUMMARY OF SINGLE OPERATOR ORSAT PRECISION FOR CO AND CO₂

Stream	Day	Species	Concentration (Vol. %)		Standard Deviation	
			Sample	Duplicate	Absolute	Relative (%)
1	5	CO	2.3	1.7	0.4	21
1	6	CO	1.7	1.2	0.4	24
1	7	CO	1.7	1.9	0.14	8
2	5	CO	2.1	2.0	0.07	4
2	6	CO	2.2	2.2	<0.05	3
2	7	CO	2.2	1.7	0.35	18
1	5	CO ₂ *	35.9	35.6	0.2	0.6
1	6	CO ₂	35.6	35.4	0.15	0.4
1	7	CO ₂	35.3	35.4	0.07	0.2
1	7	CO ₂	35.4	35.7	0.2	0.6
1	8	CO ₂	35.6	35.7	0.07	0.2
3a	7	CO ₂	75.6	77.8	1.5	2.0
3a	7	CO ₂	79.3	79.5	0.2	0.3
3a	8	CO ₂	78.7	80.0	0.9	1.1
3b	7	CO ₂	87.7	90.1	1.7	1.9
3b	8	CO ₂	84.6	84.6	<0.05	<0.1

* All CO₂ data include H₂S at about 0.2%

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TABLE 6-7. SUMMARY OF ANALYTICAL PRECISION DATA FOR IMPINGER SOLUTIONS

Impinger Solution	Stream	Test Day	Species	Method	Unit	Sample	Duplicate	Standard Absolute	Standard Relative (%)
0.1M Na ₂ CO ₃	1	3	Formate	IC	mg/L	<0.1	<0.1	N/A	N/A
	4	3	Formate	IC	mg/L	<0.1	<0.1	N/A	N/A
	1	3	Chloride	IC	mg/L	3.8	5.7	1.34	28
	1	3	Fluoride	IC	mg/L	0.1	0.1	0.01	1.0
0.1N HCl	1	2	Ammonia	Nessler	μ moles	2.22	2.22	<0.01	<1
	Blank	2	Ammonia	Nessler	μ moles	3.61	3.51	0.07	2.5
98% H ₂ SO ₄	1	2	Hydrogen Cyanide	Nessler	μ moles	58.4	59.7	0.92	1.6
	Blank	2	Hydrogen Cyanide	Nessler	μ moles	48.7	47.1	1.1	2.4
AgNO ₃ (NH ₄) ₂ S ₂ O ₈	3a	5	Mercury	AA	μg/L	<0.5	<0.5	N/A	N/A
	3a	7	Arsenic	AA	μg/L	<10.0	<10.0	N/A	N/A
	3b	5	Selenium	AA	μg/L	<10.0	<10.0	N/A	N/A
H ₂ O ₂	1	3	Mercury	AA	μg/L	1.4	0.4	0.7	79
	3b	5	Arsenic	AA	μg/L	<10.0	<10.0	N/A	N/A
	3b	7	Selenium	AA	μg/L	<10.0	<10.0	N/A	N/A

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TABLE 6-8. PRECISION DATA FOR AMMONIA/CYANIDE SAMPLING DUPLICATE TRAINS

Stream	Day	Parameter	ppmv Train 1	ppmv Train 2	Standard Deviation	
					Absolute	Relative (%)
1	2	Ammonia	<0.2	<0.2	N/A	N/A
3a	6	Ammonia	1.0	0.9	0.07	7.0
3b	4	Ammonia	1.0	0.8	0.14	16
3b	8	Ammonia	<0.2	<0.2	N/A	N/A
3a	6	Hydrogen Cyanide	0.3	0.3	<0.01*	2*
3b	4	Hydrogen Cyanide	<0.1	<0.1	N/A	N/A
3b	8	Hydrogen Cyanide	<0.2	<0.2	N/A	N/A

* Since empirical HCN ppmv values are identical, it is assumed that the average analytical standard deviations for HCN in Table 6-7 are the minimum which could be expected.

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6.5.1 Detection Limits for NH_3 and HCN in Gas Impinger Solutions

Table 6-9 presents the analytical data for HCN and NH_3 impinger samples and solution blanks. Using the variance estimated from replicate data, a t-statistic was calculated for the difference between sample and blank values for each pair of NH_3 and HCN data. The probability of observing a larger t value is shown in Table 6-9. In the case of NH_3 all sample values are greater than blank values with a high degree of statistical significance except on the test day 2. On that day the blank exceeds the sample values for Streams 1 and 2, strongly suggesting blank contamination. Rectisol Streams 3a, 3b, and 4 contain sufficient NH_3 that the blank contamination does not influence the conclusion regarding the statistical significance of NH_3 levels on test day 2.

In the case of HCN, the sample values are consistently higher than blank values with a high degree of statistical significance only in the Rectisol feed gas (Stream 1). For the CO_2 offgases (Streams 3a and 3b) and product gas (Stream 2), no consistent pattern is seen. On test days 6 and 8 it does appear that the cold stripper offgas (Stream 3a) contains HCN at levels significantly above the blank, and on day 6 the enrichment column offgas (Stream 3b) appears to contain HCN levels above the blank.

The above data may also be used to estimate the detection limits for NH_3 and HCN measured by subject sampling/analytical techniques. It is assumed that a sample must be at least three standard deviations above the blank to be reasonably certain that the difference is not simply due to sample/analytical scatter. Under this assumption, the detection limit for either NH_3 or HCN is about 0.1 to 0.2 ppmv, depending on the gas volume sampled.

6.5.2 Spike Recovery Data for Impinger Solutions

Spike recovery data for Cl, F, HCOOH , and Hg in impinger solutions are presented in Table 6-10. As indicated, no large biases are involved with any of the analyses of the impinger solutions. Spike recovery data for NH_3 and HCN are discussed in Section 6.8 in connection with analysis of aqueous samples.

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TABLE 6-9. SUMMARY OF NH_3 AND HCN GAS IMPINGER ANALYSIS DATA

Stream	Test Day	Species	Sample μ Moles	Blank μ Moles	t* Statistic	Probability of a Larger t Value†
1	2	NH_3	2.22	3.56	-12.2	<0.001†
	4		6.29	3.64	8.7	<0.001
	7		2.29	1.97	2.9	0.015
3a	4		7.01	3.64	19.6	<0.001
	6		11.0	1.24	18.4	<0.001
3b	2		4.52	3.56	4.37	0.003
	4		21.1	3.64	17.1	<0.001
	6		3.70	1.24	13.8	<0.001
4	8		4.46	2.41	9.53	<0.001
	2		6.94	3.56	10.1	<0.001
	4		5.17	3.64	6.1	<0.001
2	6		2.67	1.24	11.1	<0.001
	8		3.04	2.41	4.3	0.003
	2		1.39	1.71	-4.7	0.01†
1	2	HCN	59.06	47.91	14.7	<0.001
	4		56.23	46.64	13.2	<0.001
	7		60.69	45.87	19.4	<0.001
3a	2		45.22	47.91	-4.18	0.01†
	4		46.03	46.64	-0.95	0.35†
	6		41.13	37.92	5.81	0.001
3b	8		53.02	48.1	6.88	0.001
	2		47.12	47.91	-1.19	0.28†
	4		46.95	46.64	0.47	0.75
2	6		45.31	37.92	12.5	<0.001
	8		47.40	48.14	-1.13	0.29†
	2		46.71	46.71	0.0	<0.5

* For calculation of T statistics, replicate data for either NH_3 or HCN have been pooled to obtain a geometric mean variance (relative) for blanks and for samples. These mean variances are then applied to individual measurements for testing of statistical significance of differences of sample and blank values.

† One-sided t test unless otherwise indicated; the hypothesis is that the sample exceeds the blank.

‡ Two-sided t test; the hypothesis is that the sample differs from the blank. The blank is suspected to be contaminated when a negative t statistic is calculated.

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TABLE 6-10. SPIKE DATA FOR IMPINGER SOLUTION ANALYSES

Stream	Day	Species	mg/L Sample	mg/L Spike	% Recovery
1	3	Chloride	4.7	10	126.0
1	3	Fluoride	0.1	10	76.1
2	3	Chloride	1.2	10	82.1
2	3	Fluoride	1.1	10	80.2
4	3	Formate	<0.1	10	111.0
3b	5	Mercury	<0.0005	0.20	109.0

6.6 H₂S BY WET CHEMISTRY

On test days 7 and 8, glass bottle samples for H₂S in the Claus feed gas were collected in triplicate as a check on H₂S by GC using a thermal conductivity detector. The average relative standard deviation of these triplicate samples was 3.7%, and no statistical difference in the average H₂S content was calculated for days 7 and 8 at the 99% significance level (based on the "t" test). The reagents used in the iodometric titration of S⁼ were standardized with pure I₂ (a primary standard). During the tests, the thiosulfate titrant was checked against standard K₂Cr₂O₇ solution used for COD analysis. The thiosulfate titers based the I₂ and K₂Cr₂O₇ standards agreed within 1%, indicating no significant bias in the analytical finish for H₂S and also internal consistency between methods.

6.7 ORGANIC COMPOUND ANALYSIS BY GC/MS

Analytical replicates for GC/MS were not performed as part of the Wilmington program. However, data for samples of the CO₂-rich offgases taken on two separate days provide an estimate of the sample precision of the overall method assuming process variability is not a major factor. Table 6-11 summarizes the relative standard deviations for the seven most abundant organic compounds in these gases and for the total of chromatographable organics. For toluene and xylene, which account for more than 90% of the XAD sample loadings, the pairs of samples indicate relative standard deviations of 6

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TABLE 6-11. SAMPLE VARIANCE FOR ORGANIC COMPOUNDS IN CO₂-RICH OFFGASES

Compound	Relative Standard Deviation of Sample Pairs (%)		Approximate Relative Contribution to Total Organics (%)
	3a	3b	
Nonane	3	47	1
Decane	102	38	2
Undecane	--	--	--
Benzene	45	20	1
Toluene	15	7	45
Xylenes	9	6	46
C ₃ -benzenes	1	4	4
C ₄ -benzenes	--	--	--
Sulfur (S ₈)	--	--	--
C ₆ + sulfur	--	--	--
Naphthalene	--	--	--
Methyl Naphthalene	--	--	--
C ₂ -naphthalene	--	--	--
Bis(2 ethylhexyl) phthalate	--	--	--
Phenol	--	--	--
Methyl benzoic acid	--	--	--
Methyl phenols	--	--	--
Dimethyl phenols	--	--	--

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to 14%. For less abundant species, sample precision is much poorer, as might be expected. The sample pairs also show 1 to 7% repeatability for total chromatographable organics. These data suggest that the precision of the XAD sampling technique with GC/MS analytical finish is quite good and that stream variation is relatively small for the CO₂-rich gases.

The accuracy of the XAD absorption technique is difficult to assess. For high molecular weight compounds with high boiling points (e.g., pesticides), the resin is an efficient collector. For lower molecular weight organics, the resin acts more like a chromatographic column. Thus, total gas sample volume and species concentration influence breakthrough and collection efficiency. XAD resins samples are extracted with methylene chloride, and compounds differ in the extent to which they can be recovered by this solvent from the resin. Also, during evaporation of solvent extract, lower boiling compounds may be partially lost.

Empirical data for benzene indicates that for ppm levels in the stream to be sampled, breakthrough occurs at about 50 L/g of resin (19). Toluene would break through at about 260 L/g and p-xylene at 900 L/g. Thus, for the resin traps used at Wilmington which contain about 20 g, sample volumes of more than 1 m³ may experience benzene loss. Losses of toluene and higher molecular weight organics will be minimal up to about 5 m³. Typical SASS train sample volumes at Wilmington were 3 m³, indicating that benzene collection efficiency could perhaps be as low as 30%.

Recovery of aromatics from XAD resin is reported to be in the range of 60 to over 90%, depending on the specific compound and the concentration ranges involved (20). Thus, efficiency of recovery, like sample collection, tends to bias the values to the low side.

Another source of systematic bias in the organics analysis by GC/MS is the use of alkane standards to estimate mass loading of nonalkane organics. The fractional ion abundance on a weight basis is approximately the same for all alkanes but differs for aromatics. Generally aromatics give a stronger response than alkanes, resulting in a bias to the high side.

The biases introduced by sampling/sample recovery and by non-specific GC/MS standardization tend to counteract one another. Overall the values

reported are believed to be accurate within a factor of two. As discussed previously, the precision is much better established than accuracy for the subject samples and analytical technique. HANCOCK

In the case of the aqueous samples, the bias associated with XAD resin and GC/MS standardization were avoided since the organics were directly extracted and the compounds found were standardized against known amounts of the same substances. The GC/MS data for the aqueous samples is believed to be biased on the low side, however, since the only significant compounds found were phenolic compounds which do not completely extract with methylene chloride. Phenol is reported to be less than 50% recovered in the 100 mg/L range, and cresol about 70% (20).

6.8 AQUEOUS CONDENSATE SAMPLES

Duplicate analyses of the methanol water still bottoms were conducted for most key constituents. These data, summarized in Table 6-12, indicate that relative standard deviations for S^{2-} , SCN^{-} , NH_3 , COD, and phenols are all less than 5%. The precision levels are consistent with published data for the respective methods. Chloride and fluoride levels are too low to allow for precision estimates. Precision for TOC is dependent upon the absolute level in the sample. For TOC values less than 10 mg/L, the average relative standard deviation is 22%. At about 30 mg/L the relative standard deviation is about 10%. Duplicate data were not obtained for CN^{-} on Wilmington aqueous samples. The CN^{-} levels were sufficiently low that the entire sample volumes (500 mL) were used for analysis to improve sensitivity. At the 1 mg/L level, reported CN^{-} precision is no better than about 15% (21).

Table 6-13 summarizes the spike recovery data for the aqueous samples. For SCN^{-} , COD, and phenols the spike levels were comparable to the sample levels, while for NH_3 and formate spike levels differ greatly from the sample levels. However, the data indicate that no large bias is involved in the methods employed. No spike data were obtained for CN^{-} for the reason discussed previously.

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TABLE 6-12. ANALYTICAL PRECISION DATA FOR METHANOL/WATER STILL BOTTOMS

Day	Parameter	mg/L Sample	mg/L Duplicate	Standard Deviation	
				Absolute	Relative (%)
2	Sulfide	1.20	1.16	0.036	3.0
2	Thiocyanate	2.14	2.14	0.008*	<0.4
1	Ammonia	2.38	2.41	0.026	1.1
2	Ammonia	2.02	2.02	<0.008*	<0.4
7	Chloride	<1	<1	N/A	N/A
7	Fluoride	<0.1	<0.1	N/A	N/A
3	COD	115	121	5.3	4.5
3	TOC	34.8	31.2	3.2	9.7
4	TOC	8.1	9.8	2.3	29
5	TOC	7.9	8.1	0.18	2.2
6	TOC	5.4	8.3	2.6	38
8	TOC	6.3	5.2	0.98	17
3	Phenols	2.7	2.7	<0.9*	<3

* Estimated from rounding errors in the calculations.

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TABLE 6-13. SPIKE DATA METHANOL/WATER STILL BOTTOMS ANALYSES

Liquid Streams	Day	Parameter	mg/L Sample	mg/L Spike Level	% Recovery
5	4	Thiocyanate	2.44	0.50	92.2
5	3	Ammonia	2.54	0.1	116.4
5	8	COD	90	60	103.4
5	8	Phenols	0.5	0.4	85.3
5	6	Formate	0.7	10	75.7

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SECTION 7

DATA EVALUATION AND INTERPRETATION

A summary of the analytical data and an evaluation of the data accuracy and precision have been presented in Sections 5 and 6. In this section the internal consistency of the test data is evaluated based on the degree of material/species balance closure around the system. The balance calculations are based upon flow data provided by Texaco/Lotepro and upon characterization data obtained for the Rectisol unit input and output streams tabulated in Section 5. Also, the four streams of principal environmental interest (i.e., the CO₂-rich offgases, the H₂S-rich offgas, and the methanol still bottoms) are evaluated with regard to their content of environmentally significant compounds.

7.1 MATERIAL BALANCES

In order to provide a gross estimate of the data base quality, overall material and species balances were examined. Balances are based primarily upon gas stream flow rate data and characterization data for major constituents in each stream. Flow rate data were obtained from Texaco's in-line gas flowmeters (orifice meters) for the Rectisol feed gas (Stream 1), CO₂ cold stripper offgas (Stream 3a), H₂S-rich offgas (Stream 4), and the N₂ strip gas (Stream 6). The flow rate of the methanol still bottoms is not directly monitored, but is estimated assuming gas moisture saturation and using flow data for steam to the methanol/water separation column. The actual flow rate data from these streams are considered to be proprietary by Texaco and therefore only normalized flow data are presented in this report. Flow rate data were not available for the Rectisol product gas (Stream 2), a stream which is not of environmental significance, or for the total H₂S enrichment column offgas (Stream 3b) since a portion of the CO₂-rich offgas is drawn off for industrial use at nearby facilities.

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7.1.1 Approach to Material Balance Calculations

For balance purposes, flow rates of product gas (Stream 2) and enrichment column offgas were estimated from species balances. Two species balances must be forced to obtain estimates for the two unknown flow rates, and H_2 and CO_2 were selected for this evaluation. Hydrogen is the major constituent in the product gas, and the overall H_2 balance is essentially independent of the flow rate estimate for the enrichment column offgas. Similarly, CO_2 is the principal constituent in the enrichment column offgas, and the overall CO_2 balance is essentially independent of the flow rate estimate for the product gas. Although N_2 would in principle be an acceptable alternative to utilizing CO_2 concentrations to estimate enrichment column offgas flow, the relatively low concentration of N_2 in the enrichment column offgas is more strongly influenced by low level air contamination than is CO_2 .

The approach used for estimating material balances is illustrated by the example balance for test day 7 presented in Table 7-1. Concentrations of major stream components were normalized to 100% by adjusting the major stream component under the assumption that the largest absolute measurement error is associated with the major component. This assumption is based upon the fact that the major component in each stream is either H_2 or CO_2 , and these gases were analyzed individually by GC using separate gas injections. Thus, the combined systematic or random errors associated with H_2 and CO_2 analyses would not influence measured concentrations of other gaseous components. Concentrations of H_2 and CO_2 adjusted to total 100% are presented in the table with the associated GC analytical values indicated in parenthesis. Additionally, fixed gas analyses (i.e., H_2 , CO, CO_2 , N_2 , and $Ar+O_2$) for the feed gas and the enrichment column offgas streams were adjusted for air contamination which apparently resulted in 2 to 5% sample dilution as indicated by N_2 and $Ar+O_2$ analyses. Corrections for air contamination have been discussed in Section 5. Flow rates for the product gas and enrichment column offgas streams were subsequently estimated from H_2 and CO_2 balances using the adjusted analytical data.

As discussed in Section 6.3, the average standard deviation in replicate high level H_2 or CO_2 injections by GC is about 1% relative. It should be noted, however, that such high precision reflects repeatability of injection

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TABLE 7-1. ESTIMATED BALANCE FOR PRINCIPAL CONSTITUENTS - TEST DAY 7

Constituent	Feed Gas Stream 1		Product Gas Stream 2		Cold Stripper Offgas Stream 3a		Enrichment Column Offgas Stream 3b		H ₂ S-rich Offgas Stream 4		N ₂ Strip Gas Stream 6		Percent Balance 100 (output / input)
	moles	vol %	moles	vol %	moles	vol %	moles	vol %	moles	vol %	moles	vol %	Balance Forced ⁺
H ₂	61.9	61.9* (60.9)	61.24	96.9* (95.6)	0.0065	0.14	0.65	1.79	<0.001	<0.1			Balance Forced ⁺
CO	1.56	1.56	1.50	2.37	<0.005	<0.1	<0.04	<0.1	<0.001	<0.1			96.2
CO ₂	36.0	36.0	0.0088	0.014	3.83	81.8* (78.5)	31.04	85.83* (88)	1.13	87.6* (80.8)			Balance Forced ⁺
N ₂	0.2	0.2	0.28	0.45	0.84	18.0	4.38	12.1	0.0048	0.37	5.17	100	102.5
Ar + O ₂	0.11	0.11	0.11	0.17	0.0033	0.07	0.10	0.27	0.0006	0.05			103.5
H ₂ S	0.165	0.165	<6.3E-6	<0.1 ppmv	2.8E-5	6.1 ppmv	0.00023	6.5 ppmv	0.155	12.0			94.1
COS	0.0005	0.0005	<6.3E-6	<0.1 ppmv	9.4E-6	2.0 ppmv	0.00019	5.2 ppmv	0.00019	0.0150			76
CH ₄	0.0645	0.0645	0.063	0.10	7.5E-5	16 ppmv	0.0047	0.0130	<1.3E-6	<1 ppmv			104.8
Normalized Molar Flow Rate	100		63.20 ⁺		4.68		36.16 ⁺		1.29		5.17		100.2

* Concentration has been adjusted to yield 100% total constituents under the assumption that the largest absolute analytical error is associated with the major component. The associated GC analysis value is presented in parenthesis for comparison.

+ Product gas (Stream 2) and enrichment column offgas (Stream 3b) flow rates were estimated from H₂ and CO₂ species balances, respectively.

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only and does not reflect overall analytical precision or accuracy. This standard deviation does provide a basis, although probably overly stringent, upon which to evaluate the validity of H_2 and CO_2 adjustments for normalization of gas constituents to a 100% total. Normalized and raw H_2 data for the product gas presented in the table are seen to differ by less than 2% relative (2 analytical standard deviations) and, therefore, are in agreement within the limits of analytical precision. Indeed, of the test days for which material balances could be performed (test days 4 through 8), normalized and raw H_2 data for the product gas stream typically differed by less than about 2% relative. The largest differences were observed for the feed gas stream on test day 4 (~6% relative) and test day 8 (5% relative). Thus, the use of normalized H_2 analyses for the Rectisol feed gas and the product gas appears to be reasonable.

Normalized and raw CO_2 data from GC analyses typically differ by more than 2% relative. In the case of the cold stripper offgas this difference ranged from 2 to 6% relative for the test days on which material balances could be calculated. For the enrichment column offgas this difference typically ranged from 2 to 3% relative, although on test days 5 and 6 differences of 9 and 16% relative were determined, respectively. For the H_2S -rich offgas this difference ranged from 3 to 8% relative. While these differences between normalized and raw GC analyses for CO_2 typically exceed the 2% (relative) attributable to analytical precision, they are generally consistent with the anticipated analytical accuracy associated with CO_2 determinations by GC. Further, comparison of the GC and Orsat analyses for CO_2 indicate a slight low bias in the GC analyses, and consistently better agreement between normalized and raw Orsat analyses is observed as compared with normalized and raw GC analyses. Based upon the above considerations, the use of normalized CO_2 analyses for the CO_2 -rich offgas streams and the H_2S -rich offgas appears to be reasonable.

7.1.2 Evaluation of Material Balance Closure

A summary of material balance estimates is presented in Table 7-2 and indicates generally good closure for all the principal gaseous constituents. Material balances for CO and N_2 are all within $\pm 6\%$ of complete closure

which is less than the expected balance standard deviation of about 11% based upon analytical precision data for these gases. The product gas was the principal outlet for CO in the Rectisol feed gas; therefore, the high quality of the CO balances serves as verification for the product gas flow rate estimates. Similarly, the enrichment column offgas was the principal outlet for N₂ strip gas. Thus, the high quality of the N₂ balances tends to verify flow rate estimates for the enrichment column offgas. Based upon the analytical precision data for Ar + O₂ analyses by GC, the expected standard deviation for material balance estimates is approximately 30%. Material closures for Ar + O₂ on test days 7 and 8 are within two standard deviations of 100%. The poorer Ar + O₂ closures estimated for test days 4, 5, and 6 may indicate a lower analytical precision or accuracy during the early portion of the test period. It should be noted that since Ar + O₂ is present at very low levels in all streams analyzed, closure may be influenced by low level air contamination which would not typically influence N₂ closure or warrant correction.

TABLE 7-2. SUMMARY OF ESTIMATED BALANCES FOR PRINCIPAL CONSTITUENTS

Constituent	Test Day	Percent Balance (100 output/input)							
		1	2	3	4	5	6	7	8
H ₂	Setup	Setup/Preliminary Analyses	Preliminary Analyses	— Balance Forced* —					
CO				98	94	95	96	97	
CO ₂				— Balance Forced* —					
N ₂				95	96	107	103	100	
Ar + O ₂				220	190	242	104	66	
H ₂ S				159	--	133	94	101	
COS				56	--	70	76	--	
CH ₄				112	--	83	105	--	

* Product gas (Stream 2) and enrichment column offgas (Stream 3b) flow rates were estimated from H₂ and CO₂ species balances, respectively.

With respect to the sulfur species, material balances for H_2S are generally better than those for COS which is present at lower concentrations. Based upon analytical precision data for H_2S and COS analyses by GC, the expected standard deviations for material balance estimates are approximately 15% and 8%, respectively. Material closure for H_2S on test days 6, 7, and 8 are within essentially two standard deviations of 100%. The H_2S balance on test day 4 is substantially poorer and is considered to be indicative of problems with GC analysis of the H_2S -rich offgas during the first few test days. Material closures for COS range from 56 to 76%. These values are somewhat poorer than could be attributed to analytical scatter alone. Further, the bias suggests that either the Rectisol feed gas values are high or the Claus feed gas and/or CO_2 -rich offgas values are low. Since the same standards were used for GC determination of COS in all Wilmington samples, any bias must be related to matrix, sample size, or calculations. A review of the raw data and techniques employed did not indicate any obvious explanation for the COS results. Due to the low total sulfur levels in the feed gas during the test compared to design maximum, the previously reported COS levels do not provide any insight into the problem. In any case, the apparent bias in the balance calculations may be of little practical significance due to the very low COS levels encountered at Wilmington.

Good material balances were obtained for CH_4 , with estimated closures ranging from 83% to 112%. However, as in the case of COS, closure is somewhat poorer than would be estimated on the basis of analytical precision data (one standard deviation for the estimated balances would be about 4%). Unlike the case of COS, no apparent bias is reflected in the data.

Material balances for low level constituents such as HCN, NH_3 , Cl, F, and $HCOOH$ were also examined. Closures for these constituents are either poor or cannot be estimated since their concentrations were near or below their respective analytical detection limits (typically below about 1 ppmv). Estimated material closures for NH_3 , HCN, and Cl were 540%, <40%, and 21%, respectively. Fluoride and formate were never detected in gaseous streams although they were found in the methanol still bottoms.

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With regard to the material balance for NH_3 , the large apparent increase in NH_3 across the Rectisol unit may have resulted from process methanol and its associated NH_3 being present in the CO_2 -rich offgas samples. This would be consistent with information provided by Linde that the measured methanol contents of CO_2 -rich offgases were higher than the methanol vapor pressure for these streams calculated from column temperatures and pressures. Also, process methanol is reported to contain some NH_3 .* Some portion of the methanol in the CO_2 -rich offgases may result from evaporation of process solvent carried over into the sampling lines during the startup operations which precede the test period by a few weeks. Liquid methanol was in fact found in the sampling lines for the cold stripper offgas during test setup and purged prior to initiation of the test. However, small quantities of residual liquid methanol in the sampling lines could influence the analytical results. Alternatively, process methanol may be entrained in the enrichment column offgases on a continuous basis during operation. A distinction between these two potential alternatives cannot be made based upon available data.

HCN was found in Rectisol feed gas, product gas, and CO_2 -offgases. Due to limitations of the sampling techniques, HCN could not be determined by the impinger method in the H_2S -rich offgas. GC analyses of this stream were limited by the sensitivity of about 1 ppmv. Thus, good material balance closure could not be obtained for HCN. Unlike the case of NH_3 , process methanol contamination of the gas samples cannot account for the observed levels of HCN in the Rectisol gases. Cyanide levels measured in process methanol at Wilmington are very low* and have essentially no influence on measured HCN values in gas samples regardless of the extent of methanol contamination.

Chlorine (as Cl^-) was found in all Rectisol gas samples on test day 2. Chlorine, like NH_3 , is known to be present in the process methanol at Wilmington, and it may be that entrained methanol simply entered the impinger trains during sampling. Since the Cl levels in process methanol are proprietary information,* it is not possible to determine what portion of the measured Cl levels is attributable to residual/entrained methanol.

*Details of these data are not available since the solvent is an internal stream in the process and these data are considered proprietary by both Linde and Texaco.

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Material balance for non-methane aliphatic compounds could not be readily estimated since these compounds were often near or below detection limits in all but the H_2S -rich offgas. The fact that traces of C_3+ hydrocarbons were detectable in the H_2S offgas indicates that this stream is enriched in such compounds relative to the feed, product, and CO_2 offgases. C_2 (ethylene or acetylene), however, was found at comparable levels for both the cold stripper offgas and the H_2S -rich offgas but not for the enrichment column offgas.

Material balance for aromatics could likewise not be estimated directly since not all streams were sampled by XAD trains and/or aromatics were below detection limits by on-site GC. The GC/MS data for the resin samples indicate that the same compounds which are found to be most abundant in the feed gas (e.g., toluene, xylenes, and C_3 -benzenes) are also most abundant in the CO_2 -rich offgases although at lower concentrations. No organics other than phenols at very low levels were found in the condensate samples. These data would indicate that aromatics (i.e., toluene and xylene) tend to concentrate in the H_2S -rich offgases, provided that they are efficiently absorbed from the feed gas.

The makeup methanol flow rate and the process methanol inventory were not monitored during this test program; therefore, a methanol balance was not performed. However, measurements of methanol concentrations in the product gas and offgas streams provide a basis for estimating methanol losses from the system. Methanol analyses indicate total methanol losses in the product and offgas streams of 0.009 to 0.013 kg/kmol of Rectisol feed gas as compared with published makeup methanol requirements of about 0.0085 kg/kmol feed gas(3). From 68 to 85% of this loss was in the CO_2 -rich offgases, 12 to 29% was in the product gas, and 3 to 4% was in the H_2S -rich offgas. It should be noted, however, that there is the potential for methanol concentrations to be biased on the high side in CO_2 -rich offgas streams and/or the process gas stream. As discussed in conjunction with the NH_3 and Cl balances, this could result from evaporation of process methanol carried over into sampling piping during the startup operations which preceded testing by a few weeks. The accuracy of methanol loss estimates cannot be determined without detailed methanol balance data, and the acquisition of these data was outside the scope of this test program. A detailed methanol balance

would require long-term monitoring and very accurate flow rate measurements and would be complicated by intermittent purge and the large methanol inventory.

In summary, the degree of material closure for principal constituents is generally consistent with the analytical precision achieved during the test period and is quite good. These material balances substantiate measured and estimated flow rates for the various process/waste streams sampled. Also, they generally substantiate the analytical accuracy for fixed gases and H_2S , particularly during the final three days of testing. Somewhat poorer material closures were estimated for the trace constituents CH_4 , COS , HCN , NH_3 , and Cl , and in the case of the latter three species are thought to largely reflect (1) the fact that these compounds were typically present at concentrations at or near their respective analytical detection limits, (2) that circulating methanol which contains these species can contribute to measured values in gas sampling, and (3) that balances may be strongly influenced by the influx of shift condensate. Discrepancies in estimated closures for CH_4 and COS were greater than would be expected based on analytical precision alone. Material balances could not be estimated for non-methane organics due either to lack of complete sets of data for all streams or to levels in some streams below detection limits.

7.2 STREAMS AND CONSTITUENTS OF ENVIRONMENTAL INTEREST

All input and output streams associated with the Rectisol unit were characterized during the test period in order to enable some degree of data verification by material balance calculations. However, from an environmental standpoint the characterization data for the CO_2 -rich offgases, the H_2S -rich offgas, and the methanol still bottoms are of principal significance since they are typically of no further process use and any subsequent treatment of these streams is based largely upon environmental considerations. Of course, the H_2S -rich offgas requires some degree of reduced sulfur control for safety reasons. Characterization data for species/parameters of environmental interest relating to these streams are discussed in this section. Detailed analytical data for these streams have been presented in Section 5.

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7.2.1 CO₂-Rich Offgas Streams

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The cold stripper offgas (Stream 3a) comprised 12% of the CO₂-rich offgases while the enrichment column offgas (Stream 3b) comprised the balance. Compositions of the two CO₂-rich offgas streams are similar in most respects. The inorganic species detected in these streams are H₂, CO, H₂S, COS, NH₃, HCN, and Cl. Carbon monoxide concentrations were at or below the GC (thermal conductivity) detection limit of about 800 ppmv in the cold stripper offgases. Carbon monoxide was detected at a concentration of 800 ppmv in the enrichment column offgas. Therefore, the concentration of CO in the combined CO₂ offgas streams would be about 700 to 800 ppmv, which is consistent with the published concentration of 800 ppmv for this facility (3).

Table 7-3 presents a summary of the data for sulfur species and an estimate of sulfur species in the composite CO₂-rich offgas. The average concentrations of H₂S and COS in the combined CO₂-rich offgas were 5.4 ppmv and 4.6 ppmv, respectively, resulting in an average total sulfur concentration of 10 ppmv. These results are consistent with published data which indicate a total sulfur concentration of less than 13 ppmv in the combined CO₂-rich offgas (4).

Very low levels of NH₃ and HCN were detected in both CO₂-rich offgas streams. The concentrations of NH₃ and HCN, when detectable, corresponded to combined CO₂-rich offgas concentrations of up to 1-3 ppmv and up to 0.6 ppmv, respectively. Ammonia and to a lesser extent HCN are known to be produced in the gasification of either heavy oils or coal. The NH₃ is to a large extent condensed with moisture from the partial oxidation gas during shift conversion and the associated gas cooling which precedes Rectisol. Some portion of the HCN produced during partial oxidation is likely to be hydrolyzed during shift conversion and a portion of that which is not hydrolyzed will coabsorb with the NH₃. Thus, although NH₃ and HCN are known to be present in raw gases from partial oxidation, concentrations of these compounds are likely to be very low in the Rectisol feed gas when shift conversion precedes acid gas removal and moisture is condensed and removed prior to

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TABLE 7-3. SULFUR SPECIES IN THE CO₂-RICH OFFGASES

Test Day	Cold Stripper Offgas (Stream 3a)		Enrichment Column Offgas (Stream 3b)		Combined CO ₂ -Rich Offgas*		
	H ₂ S,ppmv	COS,ppmv	H ₂ S,ppmv	COS,ppmv	H ₂ S,ppmv	COS,ppmv	Total,ppmv
3	2	1	5	5	4.6	4.5	9.1
4	5.1	4.3	6.7	5.1	6.5	5.0	11.5
6	6.9	2.4	3.6	4.5	4.0	4.2	8.2
7	6.1	2.0	6.5	5.2	6.5	4.8	11.3
Avg.	5.0±2.1	2.4±1.4	5.4±1.4	4.9±0.31	5.4±1.3	4.6±0.35	10±1.6

*The combined CO₂-rich offgas composition has been computed from analyses of the cold stripper offgas (12% of CO₂-rich offgases) and the enrichment column offgas (88% of CO₂-rich offgases).

Rectisol. Therefore, concentrations of NH₃ and HCN in streams discharging from the Rectisol process in these applications are expected to be low. As discussed in Section 7.1, NH₃ is present in process methanol and some portion of the observed amount in the CO₂-rich offgas samples can be attributed to methanol entrainment.

Chlorine was the only trace element detected in the CO₂-rich offgases although analyses were also performed for F, Hg, As, and Se (detection limits for these elements were 0.1 ppmv or less). Chlorine was present in the cold stripper offgas at a concentration of 1.9 ppmv which corresponds to a concentration of 0.2 ppmv in the combined CO₂-rich offgas. As was the case with NH₃, some portion of the measured Cl may be attributed to entrainment of process methanol. Concentrations of volatile trace elements would be expected to be quite low at Wilmington since they are likely to be present at only low concentrations in the heavy oil feed to the POX unit. Further, since all of the POX gas is shifted, there exists the potential for removal of volatile trace elements by the shift catalyst.

The principal organic compounds detected in the CO₂-rich offgases were methanol and methane, which range from 490 to 880 ppmv and from 74 to 116 ppmv, respectively, in the combined CO₂-rich offgas. C₂ (unsaturated) and

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C₃ hydrocarbons were detected at concentrations corresponding to less than about 1.6 ppmv and 0.5 ppmv, respectively, in the combined CO₂-rich offgas. All other hydrocarbons detected were present at concentrations below 1 ppmv and contributed an additional 0.5 ppmv of organics (primarily toluene and xylenes) to the combined CO₂-rich offgas. All hydrocarbons detected in the CO₂-rich offgases were also detected in the Rectisol feed gas, which indicates that no significant levels of other volatile organics enter the Rectisol unit with the makeup methanol and that none are generated within the process. As discussed in Section 5.1, xylene and toluene in the Rectisol feed gas originate from the naphtha used to separate soot from recycle wash water in the carbon scrubber/gasification section of the plant.

Formic acid is known to be formed in high pressure, high temperature scrubbing by reaction of CO with steam. Thus, HCOOH was a target species at Wilmington in Rectisol gases. An alkaline impinger train was used to collect any HCOOH, and quantitation was by ion chromatography. Formic acid cannot be easily quantified by GC/MS in the XAD resin extracts or in aqueous samples since it is not especially soluble in the methylene chloride extractant. None of the aqueous gas impinger samples at Wilmington contained HCOOH at a detection limit of 0.05 ppmv although around 1 mg/L was found in the condensate/still bottoms. It is believed that HCOOH is largely destroyed over the shift catalyst preceding Rectisol, and any amount remaining is almost completely condensed with moisture after shift. Shift condensate is alkaline due to condensed ammonia which tends to enhance the removal of acid species such as HCOOH.

7.2.2 H₂S-Rich Offgas

Inorganic constituents of environmental interest detected in the H₂S-rich offgas are H₂S, COS, NH₃, and Cl. Essentially all of the H₂S and at least 60% of the COS in the Rectisol feed gas are present in the H₂S-rich offgas. Other sulfur species such as CS₂ and mercaptans were not detected in either the feed gas or H₂S-rich offgas during the test period. Measured sulfur concentrations in the H₂S-rich offgas ranged from 12 to 25% on test days 4 through 8; however, based upon Rectisol feed gas analyses for these days a range of total sulfur concentrations from 12% to about 18% would

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appear more reasonable. As discussed previously, this discrepancy is attributed to inaccuracies associated with GC analyses for this stream during the early portion of the test period (see Section 6.1). The sulfur concentration of the H_2S -rich offgas is lower than the published values of 25 to 35% (3). This difference is almost proportional to the lower feed gas sulfur contents measured during the test period compared to published data.

The low concentrations of other inorganic species such as NH_3 and Cl and the fact that HCN and F were not detected are consistent with the low feed gas concentrations. Ammonia was detected at concentrations up to 0.5 ppmv, while Cl was detected at 1.9 ppmv. It is suspected that at least some, if not most, of the NH_3 and Cl is attributable to process methanol entrained in the sampled gases. In any case, the presence of these constituents at such low levels in the H_2S -rich offgas is of little environmental consequence since they are not likely to influence either the performance or reliability of downstream sulfur recovery processes.

The principal organic compound present in the H_2S -rich offgas is methanol at concentrations ranging from 840 to 1000 ppmv. While methane was not found at a detection limit of 0.5 ppmv, C_2 through C_6 hydrocarbons were all detected at concentrations at 1-10 ppmv. Benzene and toluene were also detected at concentrations of approximately 0.5 ppmv each.

7.2.3 Methanol Still Bottoms

The methanol still bottoms contained low concentrations of dissolved inorganic and organic materials. Concentrations of S^{2-} , CN^- , SCN^- , NH_4^+ , Cl^- , and F^- were each a few mg/L or less. Total dissolved solids ranged from 8 to 34 mg/L. Similarly, levels of phenols (by both wet methods and GC/MS), HCOOH , and oil and grease were typically a few mg/L or less of each. However, levels of COD and TOC were found to exceed those attributable to CN^- , SCN^- , phenols, HCOOH , and oil and grease. It is possible that some process methanol is also present in the still bottoms. Low molecular weight alcohols are not readily extracted with methylene chloride, and hence the absence of such compounds in methylene chloride extracts by GC/MS does not necessarily rule out their presence in the original sample.

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It should be noted that due to the low levels of both volatile and non-volatile dissolved solids, the still bottoms can be used for process water makeup in many refinery or coal gasification applications. In such cases the stream would not constitute a primary wastewater. In the event that reuse of the still bottoms is not feasible, it can be handled along with other much larger volume wastewaters in a refinery or gasification facility with essentially no impact on design or operability of treatment units.

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SECTION 8
SAMPLING METHODOLOGY

This section summarizes the procedures used to collect gaseous and liquid samples during the Wilmington test. Gas sampling involved the collection of both small- and large-volume bomb samples and impinger and XAD resin trap samples. Samples of Rectisol condensate and process methanol were either grab(s) or composites in plastic or glass containers, some of which were pre-loaded with preserving agents for specific species. No solids samples were obtained during the tests, as the process generates no solid wastes nor uses any solid materials.

8.1 GAS SAMPLING

The sampling effort was aimed at collection of samples for subsequent analysis of the following constituents: C_1 - C_6 hydrocarbons, $>C_6$ organics, methanol, volatile heavy elements, sulfur species (H_2S , COS, RSH, CS_2 , and SO_2), other acid gases (HCN, HCl, and HF), NH_3 , fixed gases (N_2 , O_2 , H_2 , CO, and CO_2), and elemental sulfur. Gaseous streams sampled were the Rectisol feed gas, product gas, CO_2 -rich offgas (two streams), H_2S -rich offgas, and stripping gas.

8.1.1 Sample Locations

All target Rectisol gas streams had existing sampling lines, and only minor modifications were necessary to accommodate TRW sampling equipment. Generally, the modifications involved installation of valves in the existing lines to allow for pressure reduction and connection to trains or bombs with Swagelok fittings. All sample locations had existing sample purge lines (to flare) which allowed for sufficient flow/purge to obtain representative samples.

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Sampling locations were a few meters from the main stream flow for all Rectisol streams. In the case of the feed gas sampling line, its longer length and the presence of moisture in the gas stream caused concern that condensation in the cooler sampling line might influence the measurement of gaseous constituents. A somewhat different problem potentially existed with the other Rectisol gas streams. Although the gas streams are free of moisture, a small amount of entrained solvent methanol may be present which may be vaporized in the sample lines (these lines are warmer than the main streams). Thus, a potential exists for obtaining high gaseous methanol values as well as high values for volatile constituents in the circulating methanol.

8.1.2 Sampling Apparatus

Table 8-1 summarizes the gas sampling apparatus used at Wilmington. The gaseous streams are divided for sampling purposes into two categories of pressure. Those at high pressure are feed gas (Stream 1) and product gas (Stream 2) while those at medium or near atmospheric pressure are H_2S -rich or Claus gas (Stream 4), stripping gas (Stream 7), cold stripper offgas (Stream 3a), and warm stripper offgas (Stream 3b). For constituents which require large volume samples (e.g., HCN, NH_3 , $HCOOH$), large (7.6 L) single ended bombs were used for sampling of the high pressure streams. These bombs were depressurized through impinger trains at TRW's Torrance, California, laboratories for recovery of the target constituents. For the lower pressure streams, impinger trains were used onsite for large volume sample collection.

For constituents which require only small samples for GC or Orsat analyses, 0.5 or 1L teflon lined, double ended bombs were used to obtain the samples. 1L glass bottles were also used for collection of Rectisol feed and Claus feed gas samples for wet H_2S analyses. In the cases of both the small and large bombs, a given bomb was dedicated to a specific stream so that cross contamination would be eliminated.

8.1.3 Gas Sampling Procedures

Small Volume Bombs (0.5 or 1 liter)--

Samples for analysis of C_1 to C_6 hydrocarbons, aromatics, HCN, COS, CS_2 ,

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TABLE 8-1. SUMMARY OF GAS SAMPLING/SAMPLING EQUIPMENT FOR GAS STREAMS

Species*	Rectisol Gas Feed (1)	Product Gas (2)	CO ₂ -Rich Off-Gases (3a, 3b)	H ₂ S-Rich Off-Gas (4)	Stripping Gas (7)
CO, H ₂ , CO ₂ , N ₂ , O ₂ , C ₁ -C ₆ , CH ₃ OH, Aromatics	A	A	A	A	A
COS, SO ₂ , H ₂ S, HCN [†] (<200 ppm)	A	A	A	A	A
Mercaptans, CS ₂	A	A	A	A	A
NH ₃ , HCN [†]	A, B/C	A, B/C	A, C	A, C	-
HCl, HF, HCOOH	B/C	B/C	C	C	-
H ₂ S	D	-	-	D	-
>C ₆ Hydrocarbons, Sulfur	C	C	C	C	-
Volatile Trace Elements (Hg, As, Se, Sb)	C	C	C	C	-

A: Bomb - Teflon lined, 0.5L stainless steel
B: Bomb - 7.6 L aluminum

C: Gas absorption trains of various configurations depending on the species samples

D: 1L glass bottle; modified EPA Method 11 for H₂S

*CO, H₂, CO₂, N₂, O₂, C₁-C₆, CH₃OH, aromatics, COS, CS₂, SO₂, H₂S, HCN, and mercaptans are sampled for GC analysis by a single 0.5L bomb at all locations except at the Rectisol feed. There a second 0.5L sample was taken for off-site GC analysis for HCN.

[†]HCN was determined in gases by both GC and train methods.

SO_2 , H_2S , mercaptans, and fixed gases require only a single sample for each gas stream. For the Rectisol feed gas, product gas, and Claus gas where pressures are considerably above ambient, the bombs were attached to the prepurged sampling line via Swagelok connections. The bombs were then purged with sample gas for several minutes prior to collecting the sample with the purge vented to vent pipes. It was found that incomplete mixing can occur with this procedure, particularly when high flow rates are used during purging. An alternate procedure was found to be more satisfactory. The bombs were pressurized to the stream pressure, the line valves then closed, and the bomb depressurized to the vent line. This process was repeated three or more times before actually collecting the sample. The bomb valves regulating main line valves were closed, and the sample bomb was disconnected.

Since the low pressure streams could not be sampled by the modified procedure, the bombs were purged with sample gas at low flow rates for five minutes or more prior to collecting the sample.

Large Volume Bombs--

Gas samples for HCN and NH_3 and for HCl , HF , and HCOOH are collected from the high pressure Rectisol feed and product gas streams in 7.6 L single ended aluminum bombs. The bombs were later depressurized offsite for recovery of these species for analysis. The bombs were always evacuated prior to sample collection so that purging was not necessary (except for the sample line itself).

Impinger Trains for NH_3 , HCN , HCl , HF , and HCOOH --

In the low pressure Rectisol streams (CO_2 -rich offgases and Claus gas), these species were collected onsite in impinger trains. As shown schematically in Figure 8-1, NH_3 was collected in 0.1M HCl , HCN collected in 18M H_2SO_4 , and HCl , HF , and HCOOH collected in 0.1M Na_2CO_3 . Gas flow through these trains was determined by rotometers calibrated for the specific gas matrices. Appendix A includes a detailed description of the impinger train procedure.

The same types of impinger trains were employed offsite for collection of the target species from the large volume bomb samples. Flow was measured with a Dasibi model 1009-MC mass flow meter as the bombs were depressurized through the impingers. Since a small portion of the original sample (about

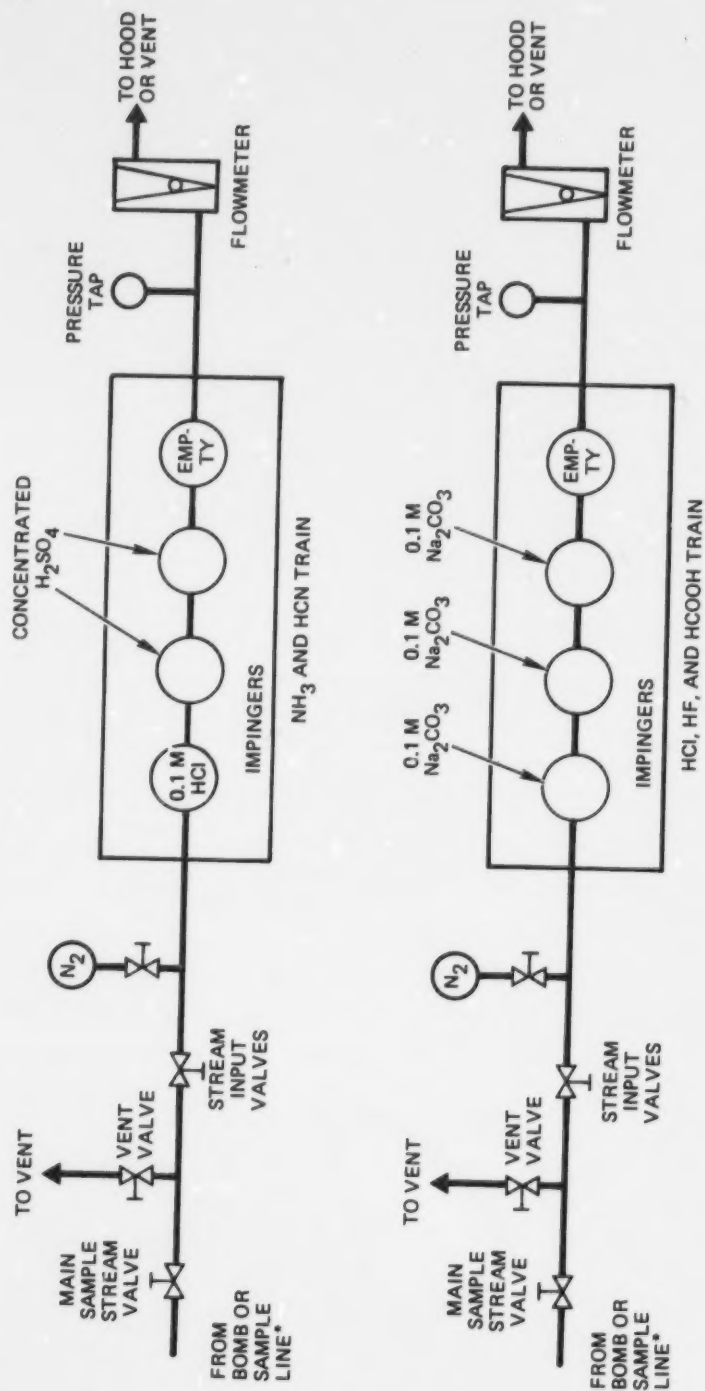
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*IN THE LABORATORY A 7.6 L ALUMINUM BOMB IS ATTACHED TO EACH TRAIN

Figure 8-1. HCl, HF, HCOOH, and HCN/NH₃ gas sampling trains configuration for on-site and laboratory gas collection

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3%) remained in the bomb at ambient pressure, the bomb was repressurized with N_2 and again depressurized through the respective impinger train. The internal volume of the bombs had been determined prior to the test, and this volume was normalized for temperature and pressure and added to the volume determined with the mass flow meter.

There was some concern about moisture in the Rectisol feed gas which might condense in the large bombs, causing a bias for NH_3 or HCN . Prior to depressurization, the bomb samples of the feed gas were placed in a water bath at $40-50^\circ C$ to vaporize any condensate (stream temperature was about $40^\circ C$), and the bombs were kept warm during depressurization. The repressurization step with dry N_2 and subsequent depressurization through the train also served to evaporate any residual moisture. After sample recovery, the bombs are evacuated for reuse.

Glass Bottle Samples for H_2S --

There was some concern prior to the test regarding the accuracy and/or precision of the GC procedure for high level H_2S determination using the thermal conductivity detector. Consequently, a second method for H_2S in the Claus feed gas was employed as a check. In this method, a grab sample of gas was collected in an evacuated flask containing a $CdSO_4$ solution. H_2S is absorbed by the reagent to form a CdS precipitate, which is subsequently filtered, acidified, and the sulfide determined by iodometric titration. The sample flask and associated apparatus are those used in EPA Method 7 for NO_x emissions (10), with 200 ml of 0.2 M $CdSO_4$ substituted for the NO_x reagent. The analytical finish is that used in EPA Method 11 (15) with the reagents adjusted for the high H_2S levels involved. Since H_2S constituted a significant portion of the Claus feed gas at Wilmington, the standardized sample volume calculated according to EPA Method 7 was corrected for the H_2S absorbed by the reagent.

Sorbent Traps and Trains for High Molecular Weight Organics and Volatile Trace Elements--

Higher molecular weight ($>C_6$) organics, volatile elements, and elemental sulfur were sampled with a sampling train consisting of an organic adsorbent trap containing XAD-2 resin and four modified Greenburg-Smith Impingers in

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series held in an ice bath. All components contacting the sample were either Teflon or glass. A diagram of the sampling train is presented in Figure 8-2.

The sample entered the sampling train through a two stage pressure and regulating/shutoff valve at the Rectisol feed/H₂ product gas locations. For other locations the regulator was not required. The sample gas passes through the XAD-2 resin where the organic components >C₆ are absorbed. Condensate is collected in an empty impinger beneath the XAD-2 resin module. After leaving the XAD-2 resin module, the sample gas passes through the first three impingers where the volatile metals are oxidized and held in solution. The H₂O₂ impinger oxidizes gases such as H₂S to prevent depletion of the persulfate impinger solutions. The last impinger (silica gel) removes the remaining moisture from the gas to protect the flowmeter.

8.2 LIQUID SAMPLING

The only liquid waste stream sampled at Wilmington was the aqueous condensate from the methanol/water still. Since the sample line was very hot and the stream was heavily laden with steam, a condensation coil was fitted to an existing valve on the blowdown line. An ice bath was used to cool the coil when samples were to be taken. Since many of the species/constituents are unstable or volatile, samples containers were preloaded with various preserving agents. Samples for inorganic species and trace elements were taken in 500 mL polyethylene bottles and samples for organic species were taken in 1 L or 10 L glass bottles. Figure 8-3 summarizes the sample collection and preservation scheme.

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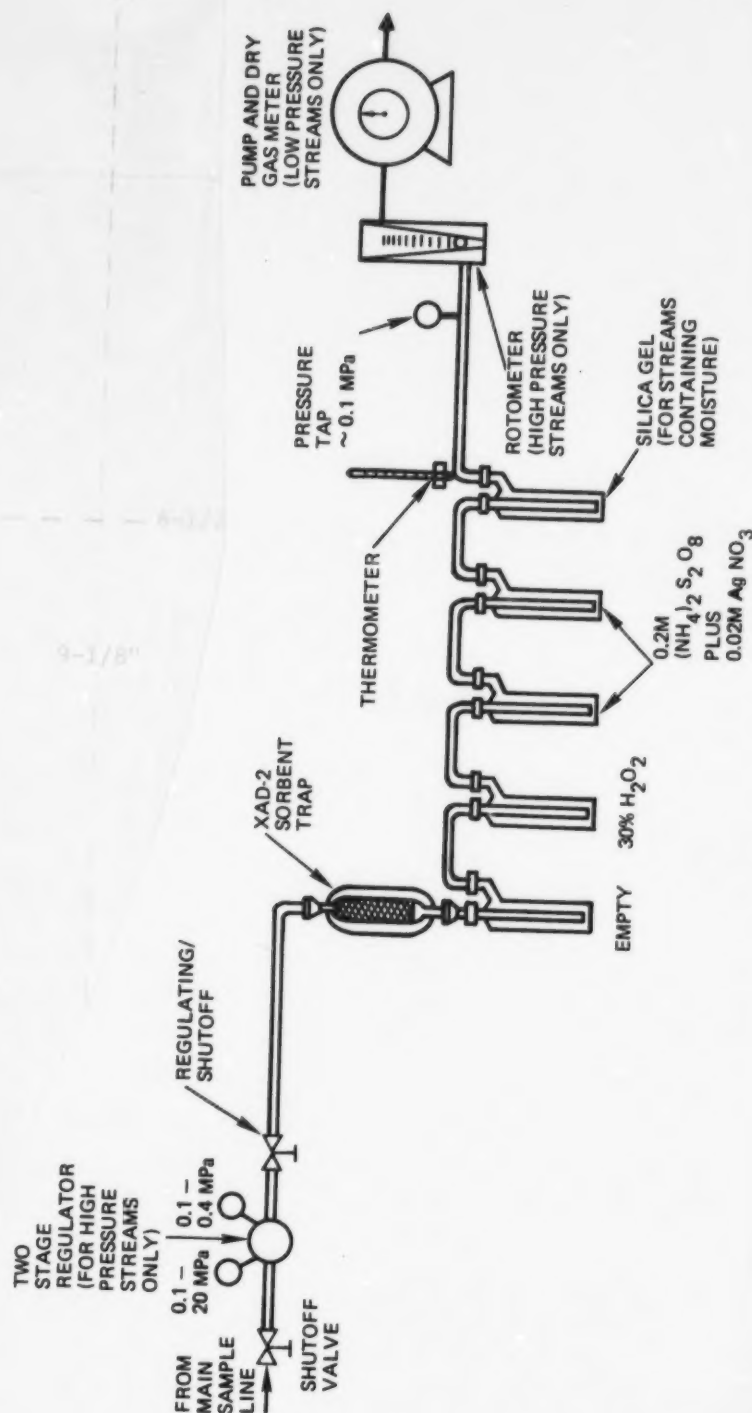


Figure 8-2. Organic and trace element sampling train configuration

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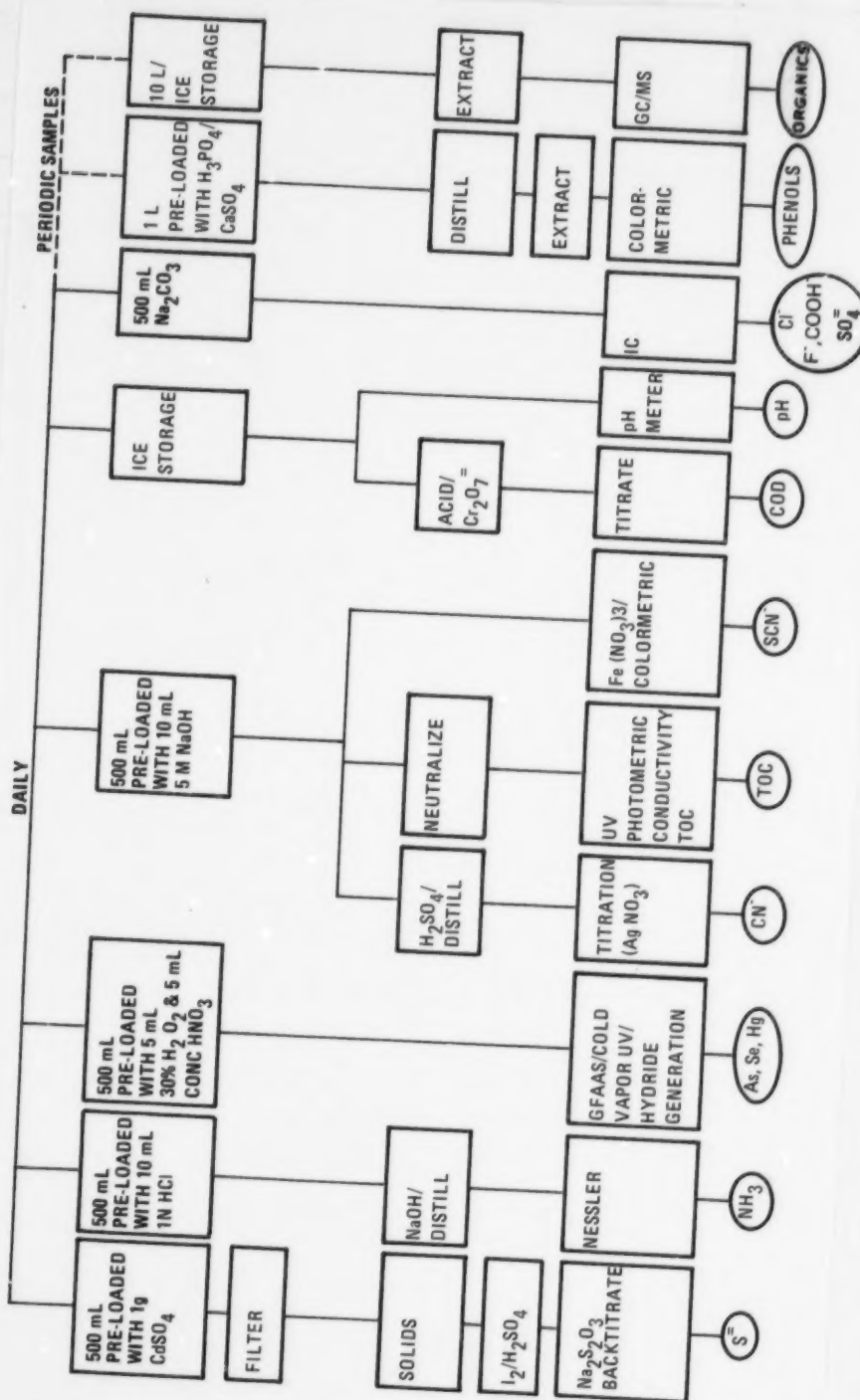


Figure 8-3. Liquid sample collection and preservation for analysis

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SECTION 9

ANALYTICAL METHODOLOGY

For the Wilmington test, sample analyses were conducted both on- and offsite. GC analyses for sulfur species and low molecular weight organics were conducted onsite in a mobil trailer. Orsat analyses for CO_2 and CO were also conducted onsite. GC analyses for fixed gases and HCN were conducted offsite, as were all wet or instrumental analyses of impingers solutions and aqueous samples. This section provides a summary of the analysis methods employed. Where standard methods have been used, only a reference(s) is given. For non-standard methods and where standard methods have been modified, key details are provided about the principles, techniques, and limitations.

9.1 GAS ANALYSES BY GAS CHROMATOGRAPHY

Analysis of samples contained in 0.5L teflon lined bombs were conducted using two onsite GCs equipped for H_2S , COS , SO_2 , CS_2 , and mercaptans and for $\text{C}_1\text{-C}_6$ hydrocarbons, aromatics, and methanol. All gas samples were loaded onto the GC columns using gas tight syringe injection. Syringe injection allows a degree of flexibility by varying sample size to maintain the detector response within the linear portion of the calibration curve. Syringe samples were taken from a free flowing stream of gas as illustrated in Figure 9-1. After the onsite GC analysis for sulfur species and hydrocarbons was performed, the 0.5L bombs were sent to offsite laboratories for fixed gases and HCN analysis.

9.1.1 Analysis of Sulfur Species

The sulfur compounds determined during this test were H_2S , COS , CS_2 , CH_3SH , $\text{C}_2\text{H}_5\text{SH}$, and SO_2 . Prior to the actual test specific analytical procedures had to be established and optimized because of the unique nature of the sample compositions expected. Available literature contained no reference to the analysis of sulfur species in the extreme dynamic range of concentrations

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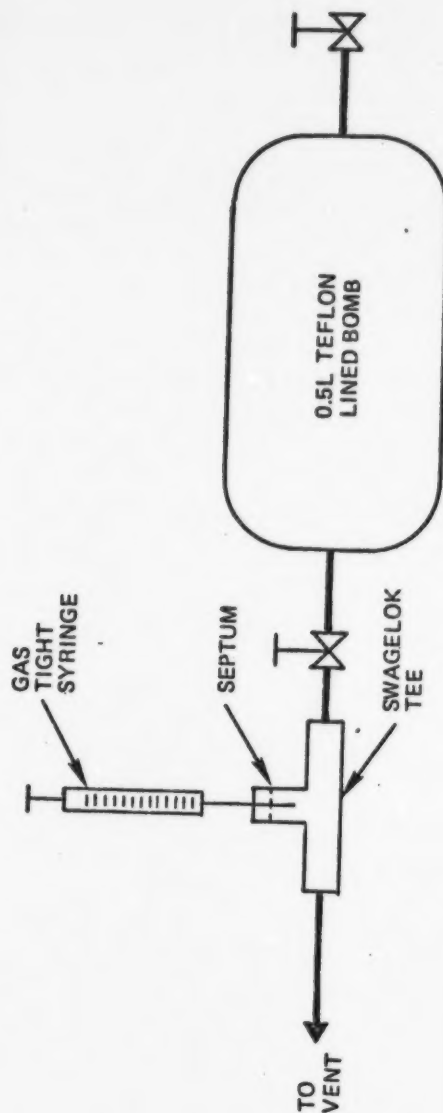


Figure 9-1. Syringe aliquot system used for GC analyses

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expected (Table 2-1). Selection of chromatographic columns was based on trace level (ppb) analyses reported in the literature. The pretest evaluation and optimization were designed to modify those procedures to work in the matrix expected. The final GC procedures selected are consistent with requirements of EPA method 15 (5).

Sulfur Species Standards--

Two standard mixtures containing H_2S , COS , CS_2 , CH_3SH , and C_2H_5SH in the concentration range expected were obtained from Scott Environmental for calibration and method optimization (Table 9-1). Injection volumes were adjusted to provide the composition range required for this study. The gas standards for all the sulfur gas species were repeatedly analyzed using manual injections with a gas tight syringe of varying volumes. Based on these measurements, it was concluded that the analysis was linear over the range of interest with a precision of $\pm 1\%$.

TABLE 9-1. SULFUR SPECIES GAS CHROMATOGRAPH GAS STANDARDS

Species	Standard Concentration (ppm)		Retention Time (min)	
	a	b	Chromosil 310	XE-60
COS	49.5	36	1.5	1.3
H_2S	4970	36	2.5	0.8
CS_2	49.8	36	5.4	7.2
CH_3SH	10	39		2.1
SO_2	--	--		6.2

Columns for Sulfur Species--

The gas chromatographic column used for the separation of inorganic sulfur species was a 0.15 m x 3.2 mm Teflon column packed with Chromosil 310 purchased from Supelco, Inc., Bellefonte, Pa. The elution order was COS , H_2S , CS_2 , and SO_2 . The temperature program selected for the optimum separation of all components was 50°C for 5 minutes programmed to 90°C at 10°C/min., then held for 10 minutes. The separation of methyl mercaptan and ethyl mercaptan required the use of a 0.15 m x 6.3 mm glass column packed with 1.5% XE-60

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and 1.0% H_3PO_4 on 60/80 Carbopack B. The oven temperature was 40°C for 5 minutes programmed to 120°C at $10^\circ\text{C}/\text{min.}$, then held for 10 minutes.

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Instruments Used for Sulfur Species Analyses--

A Tracor Model 560 gas chromatograph equipped with a flame photometric detector was fitted with the two columns described above. The operating conditions are shown in Table 9-2. Electronic integration was performed by a Shimadzu C-RIA.

TABLE 9-2. OPERATIONAL PARAMETERS FOR TRACOR MODEL 560 GC WITH FLAME PHOTOMETRIC DETECTOR

Parameter	Setting
FPD air flow	100 mL/min
H_2 flow	85 mL/min
He carrier flow	30 mL/min
Electrometer range	Square root function
Attenuation	8
Detector temperature	150°C
Injector temperature	90°C

It was determined that the concentration range expected for the H_2S -rich offgas stream was beyond the linear range of the flame photometric detector. Consequently, a Shimadzu thermal conductivity gas chromatograph was used for this analysis. This implementation eliminated detector saturation effects and brought the response vs. concentration calibration within the linear range of the detector. The operational parameters for this analysis are listed in Table 9-3. The calibration was achieved by standardization with successive dilutions of pure H_2S .

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TABLE 9-3. OPERATIONAL PARAMETERS FOR SHIMADZU GC-3BT WITH THERMAL CONDUCTIVITY DETECTOR

Recorder	Kipp & Zonen BD-40
Detector	Thermal Conductivity
Column	0.15 m x 3.2 mm O.D. Teflon column packed with Chromosil 310
Column Temperature	300C
Carrier Gas	Argon
Carrier Flow Rate	30 mL/min
Injector Temperature	300C

9.1.2 Fixed Gas Analyses

As a consequence of the stable nature of the fixed gases and the ease of transporting bomb samples, fixed gas analyses were performed offsite at TRW's laboratories. Pretest evaluation studies used synthetic gas mixtures to develop the analytical method and to solve matrix, resolution, and dynamic range problems. Standard mixtures containing H_2 , O_2 , N_2 , CO , and CO_2 within the predicted concentration ranges were obtained from Scot Environmental for calibration and methods development. H_2 and CO_2 required additional standardization with the respective pure gases.

To optimize chromatographic conditions over the dynamic range of concentrations expected, data reported for these gases were acquired on two separate gas chromatographs with three individual sets of analytical conditions. These analytical parameters are compiled in Table 9-4. The gas chromatographic columns used for the separation of the permanent gases O_2 , N_2 , CO , and CO_2 were two 0.15 m x 3.2 mm O.D. stainless steel columns packed with 0.105 mm/0.125 mm Carbosieve S purchased from Supelco Inc., Bellefonte, Pa. A second gas chromatograph with argon as the carrier gas was used for the analysis of hydrogen due to the unstable thermal conductivity measurements of hydrogen relative to helium. Argon use eliminated negative peak effects and increased overall sensitivity substantially. The elution order of the permanent gases was H_2 , N_2 , O_2 , CO , and CO_2 . CO_2 had a retention time of approximately two hours at 300C. Table 9-5 lists the retention time data for the permanent gases at the respective operating temperatures.

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TABLE 9-4. OPERATIONAL PARAMETERS FOR FIXED GAS ANALYSIS

Instrument	<u>O₂, N₂, CO</u>		<u>CO₂</u>		<u>H₂</u>	
	Shimadzu GC-3BT*	Shimadzu GC-3BT*	Shimadzu GC-3BT*	Shimadzu C-RIA†	Shimadzu GC-3BT*	Kipp & Zonen BD-40‡
Recording Device	Shimadzu C-RIA†		Shimadzu C-RIA†			
Detector	Thermal Conductivity	Thermal Conductivity	Thermal Conductivity	Thermal Conductivity	Thermal Conductivity	Thermal Conductivity
Column	Dual 0.15m x 3.2mm (O.D.) S.S. 0.105 mm/0.125 mm Carbosieve S.	Dual 0.15m x 3.2mm (O.D.) S.S. 0.105 mm/0.125 mm Carbosieve S.	Dual 0.5m x 3.2mm (O.D.) S.S. 0.105 mm/0.125 mm Carbosieve S.		0.15m x 3.2mm (O.D.) S.S. 0.105 mm/0.125 mm Carbosieve S.	
Column	300C	2250C	2250C	2000C		
Carrier Gas	Helium	Helium	Helium	Argon		
Carrier Flow Rate	30 mL/min.	30 mL/min.	30 mL/min.	30 mL/min.		
Injector Temperature	300C	2250C	2250C	2000C		

*Shimadzu GC-3BT - Gas Chromatograph with thermal conductivity detector

†Shimadzu C-RIA - Data processor with thermal sensitive printer plotter and peak integration capability

‡Kipp & Zonen BD-40 - Strip Chart Recorder - 1-10 mV input.

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TABLE 9-5. RETENTION TIMES OF FIXED GASES ON CARBOSIEVE S

Component	Column Temperature (°C)	Retention Time (Min)
H ₂	200	0.60
O ₂	30	4.59
N ₂	30	5.30
CO	30	7.98
CO ₂	225	2.40

Gas standards were repeatedly analyzed using manual injections with a gas tight syringe. Except for H₂, linear response was established over the entire concentration range tested for each of the individual permanent gases. The hydrogen response vs. concentration curve was not perfectly linear, but intercepts, slopes, and curve shape remained constant over the entire sampling interval. Twenty percent of the samples were run in duplicate to establish precision.

9.1.3 Gas Chromatographic Procedure for the Direct Determination of Hydrogen Cyanide in Gas Samples

Gaseous samples containing large amounts of hydrogen sulfide which cause problems with impinger methods were determined using a Tracor Model 560 gas chromatograph equipped with a Hall detector and a glass Porapak QS column. After sample injection the bulk of the hydrogen sulfide and carbon monoxide were vented before reaching the detector, until about 20 seconds before the hydrogen cyanide eluted. Ammonia present in large quantities prevents analysis by swamping the column but this was not a problem with Wilmington samples. Table 9-6 summarizes the GC operating conditions for HCN determination. HCN has a retention time of about 3.1 minutes under the listed conditions. Detector response is proportional to the square of the concentration. Standardization is accomplished using a 100 mg/L KCN stock solution which is acidified with 1N HCl and diluted 1/1000 with methanol. 50-500 mL injections of the diluted solution with a microliter syringe serves to establish a response curve. Typical sensitivity is 1-2 µg.

TABLE 9-6. OPERATING PARAMETERS FOR TRACOR 560-GC ANALYSIS OF HCN

Detector:	Hal1
Column:	2m x 2mm Porapak QS
Flow rate:	30 mL/min Helium
Oven temperature:	80°C
Injector temperature:	200°C
Reactor temperature:	400°C
Electrometer gain:	1 x 50
Chart speed:	20 mm/min

9.1.4 C₁ to C₆ Hydrocarbons, Aromatics, and Methanol by GC

One onsite GC was configured with a flame ionization detector to serve as a general purpose hydrocarbon analyzer. This GC/FID system (Tracor 560) using different specific columns and analysis conditions (Table 9-7) was used for C₁ to C₆ hydrocarbon analysis, aromatics, and methanol determinations in the gas streams sampled. The syringe aliquot system shown in Figure 9-1 was employed to obtain a sample for injection on most of the streams tested. For streams 3a and 3b, which were only slightly above atmospheric pressure, the sample containers were fitted with septums and the gas was drawn directly from the container using a syringe.

9.2 ANALYSIS OF IMPINGER OR BOTTLE SOLUTIONS AND AQUEOUS SAMPLES

Impinger train and aqueous samples for NH₃, HCN, Cl, F, HCOOH, As, Se, and Hg were collected at Wilmington. Analyses for these constituents were conducted offsite by wet or instrumental methods. Table 9-8, which summarizes the analytical methods employed, indicates that standard procedures were commonly used although some non-standard sample preparation steps were necessary where special preservation reagents had been employed for sample collection. Some details of specific methods are discussed below.

9.2.1 Analysis of NH₃ and HCN Impinger Solutions

The 0.1M HCl solution and 18M H₂SO₄ solutions from the NH₃ and HCN impinger trains were analyzed for NH₃ by distillation and Nesslerization. The

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TABLE 9-7. GC* CONDITIONS FOR ONSITE C₁ TO C₆ HYDROCARBON, AROMATICS, AND METHANOL ANALYSIS

Gas Species	Column Type	Carrier Gas Type Flow	Temperature Program	Injector Temp (°C)	Detector Type/Temp	Detector Flows (mL/min)		Comments
						H ₂	Air	
C ₁ -C ₆	0.15 m x 3.2 mm stainless Durapak-N-Octane Porasil C, 100/0.125mm/0.149mm	He:30 mL/min	45°C for 3 min. programmed to 75°C at 10°C/min. and held for 10 min.	100	FID/100°C	50	150	Gas tight syringe injection
Aromatics	0.15 m x 3.2 mm stainless steel 10% SP 2100 on Supelcoport 0.149mm/0.177mm	He:30 mL/min	Isothermal at 90°C	100	FID/100°C	50	150	1 mL atmospheric sampling loop
Methanol	0.15 m x 3.2 mm ID glass Chromosorb 101	He:30 mL/min	Isothermal at 75°C	180	FID/180°C	50	150	Periodic heating to 180°C to clean column

Tracor Model 560 GC

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TABLE 9-8. SUMMARY OF ANALYSIS METHODS FOR AQUEOUS CONDENSATE AND IMPINGER TRAIN SAMPLES

Species	Preservation Techniques	Reference	Summary of Procedure
pH	None	Std. Methods* Method 423, p 402	A pH meter/electrode system was used to measure pH.
Acidity	None	Std. Methods, Method 403, p 253	A filtered sample aliquot of 50 to 100 mL titrated with standardized NaOH to pH 7.0.
Ammonia (aqueous and impinger samples)	Sample collected in 0.1M HCl	Std. Methods, Method 417B, p 356	Neutralization with NaOH, distillation followed by Nesslerization.
Sulfide	ZnCO ₃ /NaOH	Std. Methods, Method 427B/D, p 446	An excess of zinc acetate/NaOH solution was pre-added to sulfide collection bottle. A known amount of sample was added directly to above solution and returned to laboratory. After filtration a known excess of acidified I ₂ was added to the precipitate and the solution back-titrated using sodium thiosulfate.
Chemical Oxygen Demand (COD)	None	Std. Methods Method 508A, p 489	A filtered sample aliquot was reacted with a standard amount of chromic acid. The excess unreacted dichromate is then back-titrated with ferrous ammonium sulfate.
Cyanide (aqueous samples)	0.1M NaOH	Std. Methods Method 412, p 319	Calcium hydroxide and lead acetate are added to an aliquot of filtered sample. The resulting solution is filtered to remove precipitated carbonate and sulfide. The filtrate is acidified and distilled, and the evolved hydrogen cyanide is collected in an absorbing (NaOH) solution. A trapping scrubber containing 3M Pb(NO ₃) ₂ at pH 3 is placed ahead of the NaOH containing scrubber. This is to remove evolved sulfide from the distilling gas stream. The absorbing solution is titrated with standard silver nitrate reagent using p-dimethylaminobenzalrhodamine indicator.
Cyanide (impinger solutions)	Sample collected in 18M H ₂ SO ₄	Std. Methods Method 417B, p 356	Neutralization with NaOH, distillation followed by Nesslerization

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TABLE 9-8. (CONTINUED)

Species	Preservation Techniques	Reference	Summary of Procedure
Thiocyanate	None	Std. Methods, Method 412 K, p 330	Sample was acidified with HNO ₃ to a pH <2. Ferric nitrate was added to form a red colored complex with the SCN ⁻ . The SCN ⁻ concentration was determined colorimetrically.
Total Dissolved Solids (TDS)	None (filtrate from TSS used)	Std. Methods, Method 208A, p 92	A well mixed filtered sample was evaporated in a weighed dish and dried to constant weight at 180°C.
Total Organic Carbon	Cooled to 40°C	Std. Methods, Method 505, p 471	Total organic carbon was determined by UV oxidation of organic carbon using a Sybron/Barnstead Photochem Organic Carbon Analyzer.
Oil and Grease	Cooled to 40°C H ₂ SO ₄ to pH 2	Std. Methods, Method 503 C, p 463	Acidified sample was extracted three times with trichlorofluoroethane. The extracts are dried over anhydrous sodium sulfate and combined. The solvent is distilled using a water bath at 70°C. The flask containing the distillate is desiccated and weighed.
Cl ⁻ , F ⁻ , and COOH ⁻	1) Filtered only 2) Filtered cool to 40°C	Dionex appl. [†] notes #11	These anions were determined using a Dionex Model 16 Ion Chromatograph. Anions were separated on a weak anion exchange column, and then converted to their respective acids on a suppressor column. The suppressor column also served to reduce the background conductivity of the sample. Quantitation was accomplished using a conductivity detector.
Phenols	Cool to 40°C, H ₂ PO ₄ to pH <4, 1.0 g CuSO ₄ /L	Std. Methods, Method 510 A and 510 B, p 510	Samples were acidified with phosphoric acid and steam distilled. The distillate was reacted with 4-aminoantipyrine, and the colored antipyrine dye was extracted into chloroform. Absorbance was measured at 460 nm.

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TABLE 9-8. (CONTINUED)

Species	Preservation Techniques	Reference	Summary of Procedure
Trace Organics	Cool to 4°C	EPA Method 1624 [†]	The water samples were extracted with methylene chloride and concentrated to a known volume (1 mL). Methylene chloride extracts were analyzed by GC/MS equipped with a DB-5 coated fused silica capillary column (30m x 0.032mm I.D.).

*Reference 9.

†Reference 11.

‡Reference 15.

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distillation apparatus and procedure were slightly modified to prevent bumping and glassware breakage, as described in Appendix A.

9.2.2 Analysis of COOH^- , Cl^- , and F^- in Carbonate Impinger Solutions

The sodium carbonate impinger solutions were analyzed for COOH^- , Cl^- , and F^- by ion chromatography with no species pretreatment. Formate is eluted with sodium borate, and Cl^- and F^- are eluted with sodium bicarbonate. Appendix B details the ion chromatographic method.

9.2.3 Analysis of As, Se, and Hg

Impingers from trace element trains consisted of H_2O_2 and ammonium persulfate solutions. These solutions were split for analysis of As and Se and of Hg, respectively. Arsenic and selenium determinations were made with an Instrumentation Laboratory (IL) Model 555 graphite furnace atomizer in conjunction with an IL Model 551 or 951 atomic absorption spectrophotometer. Sufficient $\text{Ni}(\text{NO}_3)_2$ was added to the samples to reach 1% nickel (13). Nickel stabilizes the arsenic and selenium as nickel arsenide and selenide, allowing high ash temperatures (1100°C and 900°C, respectively). Calibration curves were run to establish the linear absorbance range for each element. All samples were low in arsenic and selenium so standard additions giving approximately 25% and 50% of the linear absorbance range were used. The absorbance of each sample and its standard additions were used in a least squares calculation of a best fit line. The x-intercept represents the concentration of the analyte in the original sample. The detection limit in the peroxide impinger solution was 2 µg/L As and 4 µg/L Se. Due to high background, the detection limit for selenium was 10 µg/L in the ammonium persulfate impinger. The arsenic detection limit was 2 µg/L except in the ammonium persulfate impinger from Stream 1, Day 3 which showed extreme data scatter resulting in a detection limit of 50 µg/L for this sample.

For Hg analysis, both the peroxide and persulfate impingers required pretreatment. The presence of the silver catalyst in the ammonium persulfate solution has been shown to result in low Hg recoveries. Precipitation of silver with chloride and filtration effectively removes this interference. The detection limit was 0.5 µg/L after this pretreatment. The peroxide impinger solution interferes by consuming the stannous chloride reducing agent. This

problem is circumvented by decomposing the excess peroxide with permanganate prior to analysis. This procedure results in a detection limit of 1 $\mu\text{g/L}$.

Mercury was determined in the pretreated solution using the cold vapor atomic absorption method. Samples and standards were analyzed by placing 20 mL in the vapor generator. Ten mL of 1:1 HNO_3 , 6 mL of 1:1 H_2SO_4 , and 5 mL of 20% SnCl_2 reducing agent were sequentially added to the generator. The mercury vapor was purged out of the generator, through a soda lime drying cartridge and into a quartz cell, where the atomic absorption was measured. Standardization was accomplished by adding known amounts of mercury (0.02 - 0.2 μg) and recording the peak heights. The limit of detection was 0.2 $\mu\text{g/L}$.

9.2.4 Analysis of H_2S Gas Bottle Solutions

Samples for gaseous H_2S in H_2S -rich offgas (Stream 4) were obtained in glass bottles preloaded with a cadmium sulfate solution. The solutions containing precipitated CdS from these glass sampling bottles were analyzed according to the EPA Method 11 analytical procedure, modified for the high H_2S levels involved. A solution of 0.2 M sulfate was used in place of the specified 0.02 M absorbing solution and a total of 200 mL was employed in the EPA Method 7 sampling bottles. An aliquot of this 20 mL was acidified and titrated iodometrically, using a magnet stirrer to ensure a representative aliquot with the pipeting of a solids laden solution. The Method 7 and Method 11 procedures are detailed in Appendices E and F, respectively.

9.3 OFFSITE ORGANIC ANALYSIS PROCEDURES

Both liquid and gas samples were taken in the field for organic analysis in the laboratory. Also, aqueous condensate samples of the methanol still bottoms were obtained for organics analysis. Gas samples were taken from the feed gas and the CO_2 -rich offgas streams using a collection system containing XAD-2 resin to absorb volatile gases whose boiling points were above n-hexane. Three general types of analyses were performed on these samples:

- Level 1 survey analysis (13)
- Level 2 compound analysis (14)
- Priority pollutant analysis (15)

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Level 1/Level 2 analysis refers to a phased approach to organic analysis developed by the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory in Research Triangle Park, N.C. The Level 1 procedures are directed at producing qualitative and some quantitative information about the samples so that more specific procedures (Level 2) can be used to identify and quantitate individual compounds. Priority pollutant analyses refer to the determination of specific compounds required by the National Pollutants Discharge Elimination System.

9.3.1 Sample Preparation

Two types of samples were collected for later organic analysis. They were the XAD-2 resin from the gas absorption trains and the aqueous solution from the methanol still bottoms. Solid samples like the XAD-2 resin are extracted using methylene chloride in Soxhlet extractor. Liquid samples (in this case 750 mL) first have their pH adjusted to pH 12 and then are extracted with methylene chloride using a separatory funnel. The base/neutral compounds are obtained from this extraction. Acid is then added to some aqueous sample to reduce the pH to 2 and re-extracted with methylene chloride to recover the acidic compounds. However, it was determined through an independent wet chemical analysis (9) that significant levels of phenols were present. In order to improve the phenol recovery from the aqueous samples, the order of pH adjustment was changed to acidic (pH 2) followed by basic (pH 12) extraction. This had the effect of producing acid/neutral and base fractions.

Once the extracts were obtained from the XAD-2 resin and the aqueous samples, they were separately concentrated to 1 mL using a Kuderna-Danish evaporator with a 3-ball Synder column. All of the organic analyses were performed on these concentrated samples.

9.3.2 Level 1 Organic Analysis

In the Level 1 analysis of the extracts, hydrocarbons in the boiling point range of 100° to 300°C are quantified using gas chromatography (GC). This procedure is called total chromatographical organics and generally

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is run on a GC with a flame ionization detector and a packed column (OV-101 on 0.125 mm/0.149 mm Supelcoport). In this case a GC/MS system with a fused silica capillary column was used. Operating conditions for this system are found in Table 9-9. By using a GC/MS system, equivalent data to the Level 1 TCO analysis can be obtained while specific compound information is being collected using the mass spectrometer. Quantitative calibration of the TCO procedure is accomplished by use of mixtures of known concentrations of the normal hydrocarbons C_8 , C_{12} , and C_{16} . The quantitative calibration standards were prepared to cover the concentration range to be studied. Retention time limits corresponding to the TCO range of boiling points are defined by the peak maxima for n-heptane (C_7 , bp 98°C) and n-heptadecane (C_{17} , bp 303°C). Retention time windows for the individual n-alkanes were set half way between the individual n-alkane peak maxima. The total ion current integrated over the individual retention time windows including a specific n-alkane was reported as that n-alkane. The Level 1 TCO data were output after appropriate dilution of gas volume corrections as $\mu\text{g}/\text{m}^3$ of C_7 to C_{17} n-alkanes.

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TABLE 9-9. SUMMARY OF GC/MS OPERATING CONDITIONS

<u>System:</u>	Finnigan 4000
<u>Column:</u>	Wide bore fused silica capillary column (30m x 0.33 mm ID) coated with SE-54 (methylphenylvinyl silicone)
<u>Temperatures:</u>	SE
	- Injector - 250°C
	- Jet Separator - 250°C
	- Source - 280°C
	- Transfer lines - 250°C
	- Temperature program - 50°C for 2 minutes followed by a temperature increase of 10°C/min to 250°C and a 17 minute hold at 250°C
<u>Column Flowrate:</u>	0.80 m/sec (He carrier gas)
<u>Mass Scan Rate:</u>	40 to 540 amu every 2 seconds

Gravimetric (GRAV) analysis is employed to provide a measure of those compounds whose boiling point is above 300°C. In this procedure a sample of concentrated extract is evaporated to dryness in a pre-tared aluminum dish and dried to constant weight (± 0.1 mg) in a desiccator over silica gel or Drierite. The sample aliquot is varied to contain approximately 10 mg of organic matter.

At this point the Level 1 procedures set threshold concentrations based on the sum of the TCO and GRAV analyses for further analysis of the sample. These concentrations are:

- Gas streams (XAD-2 resin) - 0.5 mg/m^3 computed at the source
- Liquid streams - based on a 10 mL concentrated volume, a 1 mL GRAV aliquot, and a 5 μL TCO injection; ≥ 15 mg sum of TCO and GRAV analyses are required for additional analyses

Since the gas and the aqueous streams did not exceed these levels, no further Level 1 analyses were performed on the samples taken at Wilmington.

9.3.3 Level 2 Organic Analysis

Level 2 organic analyses are designed to identify specific compounds. Almost any type of organic analysis can be performed, but generally gas chromatography with a mass spectrometer is employed to measure volatile compounds. In this program, the methylene chloride extracts of the aqueous solutions and XAD-2 resin were analyzed for organic compounds. In this case data from the GC/MS TCO analysis performed under the Level 1 survey analysis were reinterpreted for the purpose of identifying specific organic compounds. The results of this data interpretation were reported as $\mu\text{g/m}^3$ (XAD-2 resin) or $\mu\text{g/L}$ (aqueous sample) of the compounds found.

U.S. EPA Method 625 (base/neutrals, acids, and pesticides) was used to analyze the methylene chloride extracts from the aqueous samples. As mentioned earlier, the order of extraction is supposed to be pH 12 followed by pH 2. Because of the known presence of phenols the order of pH extraction was reversed to ensure removal of all of the phenolic compounds in the first extraction. Figure 9-2 depicts the sample preparatory scheme. Another modification of the procedure was the use of the fused silica capillary column.

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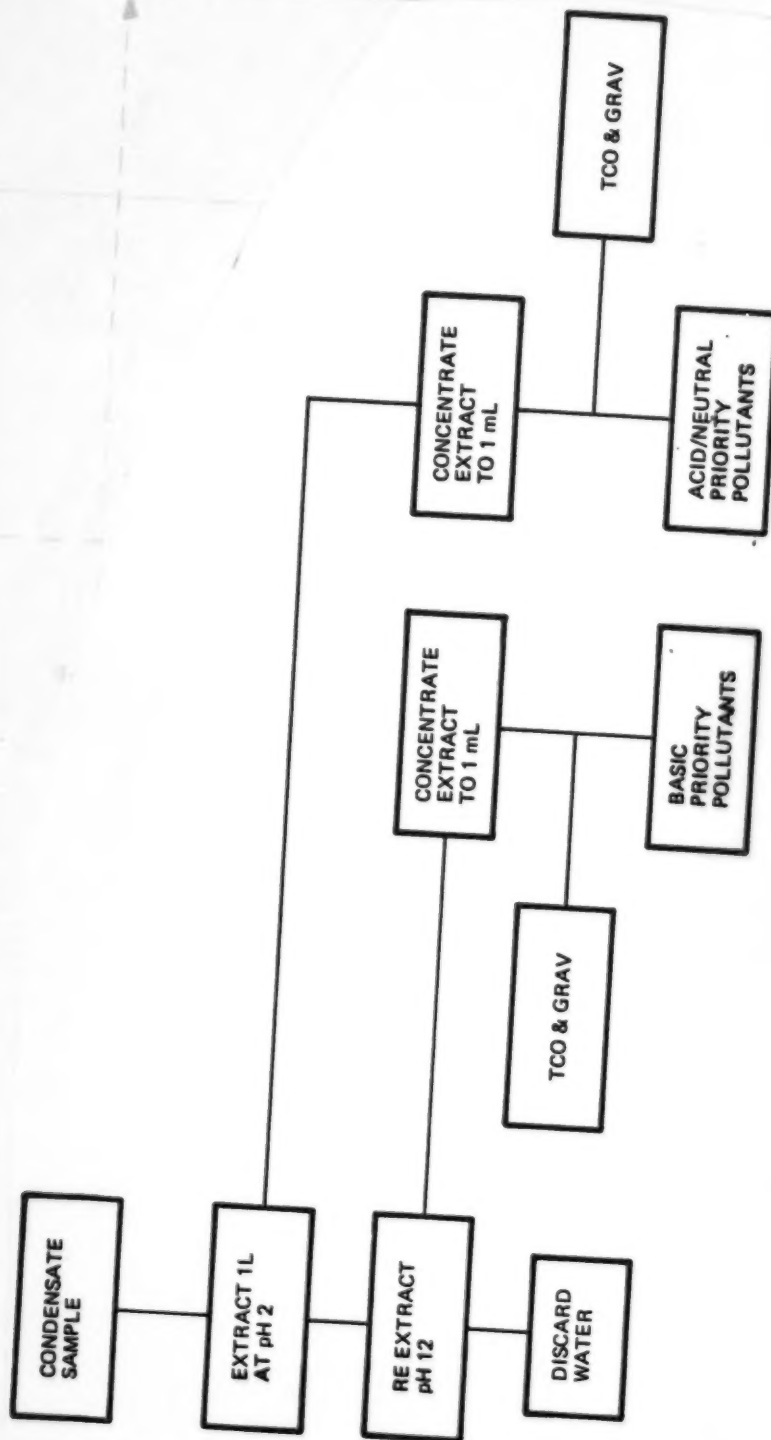


Figure 9-2. Summary of organic analysis for aqueous condensate samples

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The compounds commonly sought in Method 624 are listed in Appendix D. Using a computerized library of compounds, the GC/MS scans from the Level 1/Level 2 analyses were reviewed for the presence of these compounds. The results of the analyses are reported in Section 5.4.

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APPENDIX A

PRETEST HCN AND NH_3 TEST METHODS VERIFICATION

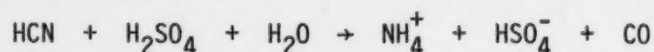
Although all of the species of interest in the Wilmington test have been sampled and analyzed in streams from other industrial facilities, the Wilmington test presented special problems due to both the high CO_2 and/or H_2S levels in the gases and to the low levels of the target species involved. In particular, the sampling techniques for HCN and NH_3 required pretest verification.

Acid gases such as HCN are commonly collected in gas impinger trains containing strong base (KOH or NaOH) (13). When the matrix is an inert gas such as N_2 , and sufficient gas/liquid contact is provided in the impingers, essentially quantitative absorption can be obtained. At Wilmington, the gas matrix contains H_2S which will compete with the relatively weak HCN for the available base. At the high levels encountered at Wilmington, CO_2 and H_2S absorption could have lowered the pH of the absorbing base solution to levels where HCN was not effectively absorbed.

During a previous field sampling effort, test personnel had noted several problems in sampling for HCN and in subsequent cyanide analyses. In that instance, the gas stream contained about 10% CO_2 and 1% H_2S , while HCN levels were in the 10-300 ppmv range. HCN recovery was found to be related to the impinger design and sampling rate, indicating that gas/liquid contact was important. Slowing the sampling rate to achieve better gas liquid contact, however, resulted in nearly quantitative CO_2 and H_2S removal along with HCN. With the large volume samples needed for sufficient sensitivity for HCN, the absorbed CO_2 and H_2S lowered the pH to levels which were too low for complete HCN absorption (i.e., less than pH 9). The absorption of CO_2 , and to a lesser extent H_2S , also reduced the volume of gas exiting the impinger train. Thus, accurate metering of the gas volume passed through the train would not be possible unless corrections were made for the CO_2 and H_2S absorption. Absorption of H_2S in caustic impinger solutions also created a high sulfide matrix

for subsequent cyanide analysis. Acidification and subsequent distillation during the standard cyanide analysis resulted in H_2S carryover and interference in the cyanide analytical finish. The sulfide interference was found to be largely eliminated by the use of a lead acetate scrubber between the cyanide distillation apparatus and the HCN absorbing solution.

Due to these fundamental limitations of the caustic absorption approach, an alternate approach was sought. The most promising method found from the literature (Welcher, F.J.) (2) was based upon the collection of HCN in concentrated (18 M) sulfuric acid followed by determination of the NH_3 formed by the hydrolysis reaction:



Since any NH_3 in the gas would also be collected in the concentrated H_2SO_4 , a sampling train consisting of a dilute acid impinger(s) for NH_3 collection followed by concentrated sulfuric acid for HCN collection (hydrolysis) serves to eliminate the NH_3 interference and also allow for NH_3 collection and quantification. The analysis of both the dilute and concentrated acid solutions is by the Nessler procedure after neutralization and distillation of the NH_3 .

The laboratory apparatus for evaluation of the sulfuric acid HCN collection method consisted of three units: a matrix gas source, an inlet port or generator of analyte gas, and an impinger system for analyte recovery. The apparatus is shown schematically in Figure A-1. The matrix and standard gas was commercially obtained compressed gas cylinders of N_2 , CO_2 , 2.1% H_2S in N_2 , and 2041 ppmv NH_3 in N_2 . Flow from each individual cylinder was controlled by a two-stage regulator, needle valve, and rotometer. The rotometers were calibrated with a bubble flow meter for each type of gas. Teflon tubing and Teflon or stainless steel fittings were used to construct a gas blending system, using the matrix gases as the carrier or purge gas. The matrix gases were passed through the HCN generator, which was upstream from the NH_3 gas inlet to premix the HCN gas with the nitrogen/matrix gases prior to blending with NH_3 . The inlet port for the introduction of the ammonia standard was a septum which fit in one leg of a "tee" fitting. A variable speed syringe pump and a gas-tight syringe were used to inject anhydrous ammonia through the septum at a constant rate. The other legs of the tee were connected to the HCN generator and to the impinger system (Figure A-1).

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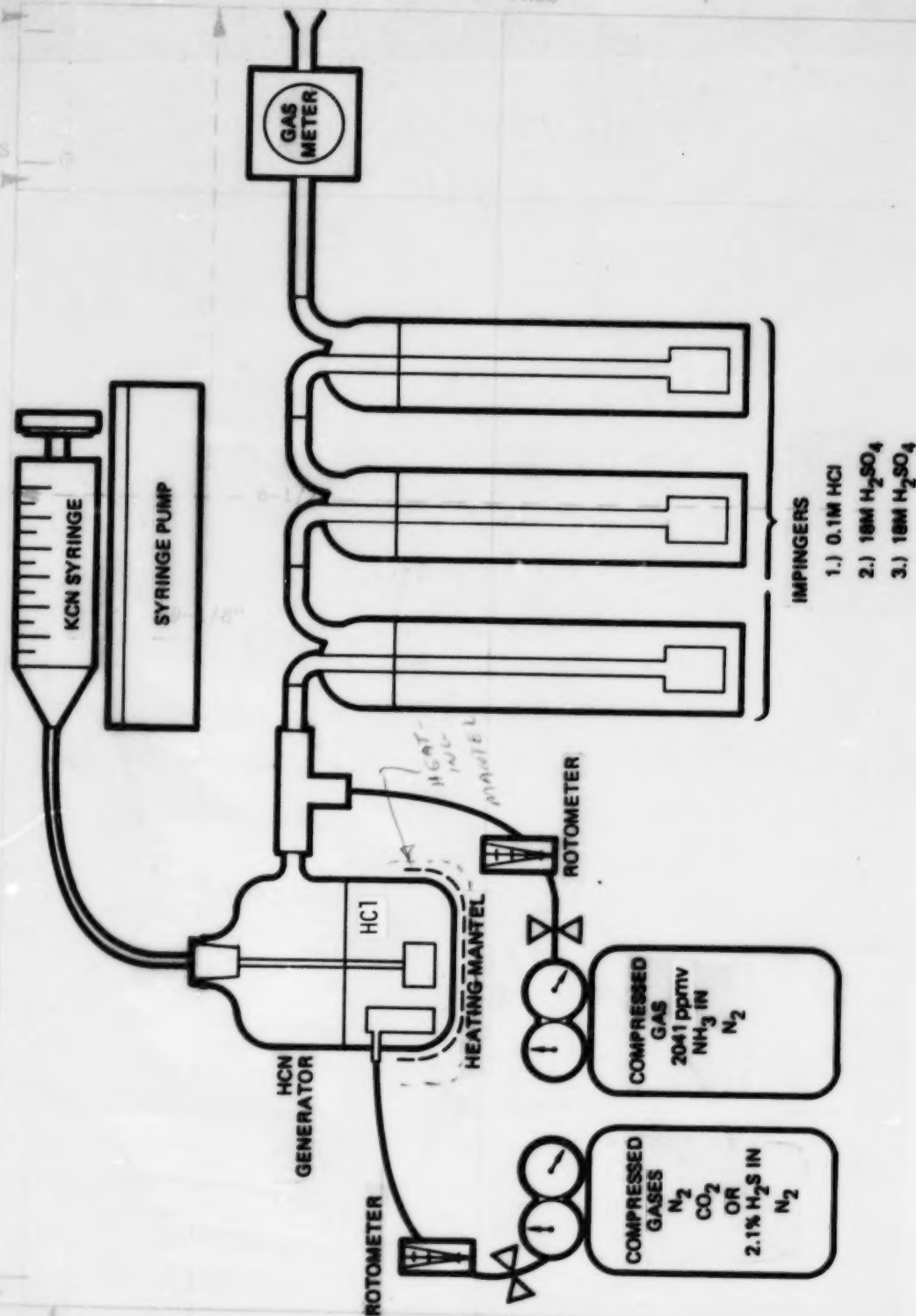


Figure A-1. Laboratory apparatus for testing the H_2SO_4 method for HCN absorption

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The gas generator for cyanide was a 150 mL Pyrex flask with a fritted inlet near the bottom, a stoppered top, and a side arm outlet. Hydrogen cyanide was quantitatively generated by the addition of a standardized solution of potassium cyanide to a 0.1M solution of HCl. The KCN solution was added from a syringe using a syringe pump to deliver a constant rate. The HCl was kept at 90°C by a heating mantle jacket.

Using the apparatus in Figure A-1, a series of experiments was conducted to determine the performance of the H_2SO_4 method for HCN and NH_3 collection. The first set of experiments was aimed at determining whether any HCN would be collected in a dilute acid impinger preceding a concentrated H_2SO_4 impinger. In the initial experiment, approximate test gas concentrations of 50 to 250 ppmv were used to study the recovery in the impinger system. The results of experiments 1A, 1B, and 1C indicate that both 10% and 1% H_2SO_4 will collect a few percent of the HCN in the feed gas, as shown in Table A-1. The data in the table also indicate that at least two impingers of 18M H_2SO_4 are necessary under the test flow conditions to realize high percentage recoveries of HCN. CO_2 appears to have a small influence on HCN recovery compared to N_2 in the H_2SO_4 impingers. Experiments 1D and 1E show that one 0.1M HCl impinger collects only about 2% of the HCN in the feed under the test flow conditions while one 1M KOH impinger quantitatively collects HCN in an N_2 matrix.

The hydrolysis of HCN to NH_3 in dilute H_2SO_4 potentially limits the use of the published procedure for simultaneous HCN and NH_3 determination. A static experiment was conducted to assess the hydrolysis of HCN as a function of H_2SO_4 concentration. The data from this experiment as shown in Table A-2 agree with the results of the impinger experiment discussed above.

A second set of experiments was aimed at determining whether the matrix has any effects on the efficiency of NH_3 collection in dilute acid impingers. The results of these experiments, as summarized in Table A-3, show that a single impinger of either 0.1M HCl or 1% H_2SO_4 is sufficient to quantitatively recover NH_3 in an N_2 matrix and that CO_2 has no apparent effect on collection efficiency. H_2S appears to have a small effect on NH_3 collection efficiency when only one dilute acid impinger is used.

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TABLE A-1. THE COLLECTION OF HCN IN ACID AND BASE IMPINGER TRAINS

	Matrix Gas Flow	Impinger 1	Impinger 2	Impinger 3	Impinger 4
Experiment 1A	1L/min N ₂	10% H ₂ SO ₄	18M H ₂ SO ₄	18M H ₂ SO ₄	None
Micromoles HCN*	Not determined	13.2	151	13.6	
% of total [†]	--	7.4	84.9	7.7	
Experiment 1B	0.6L/min N ₂ 0.4L/min CO ₂	10% H ₂ SO ₄	18M H ₂ SO ₄	18M H ₂ SO ₄	None
Micromoles HCN*		18.0	113	25.7	
% of total [†]		11.5	72.1	16.4	
Experiment 1C	0.6L/min N ₂ 0.4L/min CO ₂	1% H ₂ SO ₄	1% H ₂ SO ₄	18M H ₂ SO ₄	18M H ₂ SO ₄
Micromoles HCN*		31.8	5.6	220	58.5
% of total [†]		10.0	1.8	69.6	18.6
Experiment 1D	1L/min N ₂	0.1M HCl	1M KOH	None	None
Micromoles HCN*		1.9	105		
% of total [†]		1.8	98.2		
Experiment 1E [‡]	1L/min N ₂	0.1M HCl	1M KOH	None	None
Micromoles HCN*		2.1	107		
% of total [†]		1.9	98.1		

* Recovered HCN basis

[†] Measured as NH₃ by Nesslerization

[‡] Repeat of Experiment 1D

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TABLE A-2. HCN HYDROLYSIS IN SULFURIC ACID SOLUTIONS*

Concentration of H ₂ SO ₄ (wt %)	Percent of HCN Hydrolyzed to Ammonia
98	97.2/97.7
90	60.9
77	16.6
65	13.7
10	7.4

*88.7 micromoles of cyanide (KCN solution) added to 25mL of acid and allowed to react 15 min.

A third set of experiments was conducted to determine the HCN collection efficiency of 18M H₂SO₄. The data in Table A-4 show that two impingers are necessary for high HCN collection efficiency in N₂ and that CO₂ has only a small inhibitory effect on HCN hydrolysis. H₂S at the 2% level in N₂ has no effect on HCN absorption.

The subject experiments establish that a train consisting of one impinger containing 25 mL of 0.1M HCl and two impingers each containing 25 mL of 18M H₂SO₄ is adequate to separately collect 95% or more each of the NH₃ and HCN present in matrix gases containing N₂, CO₂ up to 40%, and H₂S up to 2%. Sampling rates of about 1 L/min are allowed but fritted glass gas dispersion tubes are necessary. The procedure can technically be considered verified only for 10-200 ppmv NH₃ or HCN range, although there is no reason to suspect that lower levels would present new problems.

When H₂S is present in the sample gas at levels above 2%, elemental sulfur is formed in the 18M sulfuric acid impingers in amounts that quickly clog the solutions and the frits. Consequently, the procedure can be used with high H₂S streams only when the sample gas also contains relatively large amounts of HCN (at least 0.1%). Otherwise, the large sample volumes required for HCN analytical sensitivity are inconsistent with the physical limitations imposed by precipitated sulfur. Thus, the impinger method was not used at Wilmington to quantify HCN in the H₂S-rich Rectisol offgas (Claus feed gas). An alternate

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TABLE A-3. COLLECTION OF AMMONIA IN ACID IMPINGER TRAINS

	Matrix Gas Flow	Impinger 1	Impinger 2	Impinger 3	Impinger 4
<u>Experiment 2A</u>	1L/min N ₂	0.1M HCl	0.1M HCl	0.1M HCl	
Micromoles NH ₃		58.8	<0.6	<0.6	None
% recovery*		<99	<1	<1	--
<u>Experiment 2B</u>	0.6L/min N ₂ 0.4L/min CO ₂	1% H ₂ SO ₄	1% H ₂ SO ₄	1% H ₂ SO ₄	18M H ₂ SO ₄
Micromoles NH ₃		81.1	<0.6	<0.6	0.8
% recovery*		99	<1	<1	
<u>Experiment 3B</u>	1L/min 2% H ₂ S in N ₂	0.1M HCl	18M H ₂ SO ₄	18M H ₂ SO ₄	None
Micromoles NH ₃		68.0	5.7	<0.6	
% recovery*		92.3	7.7	<1	

* Input NH₃ not separately measured, percent refers to the total measured in impingers.

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TABLE A-4. COLLECTION OF HCN IN 18M H₂SO₄ IMPINGER TRAINS

	Matrix Gas Flow	Impinger 1	Impinger 2	Impinger 3	Impinger 4	Impinger 5
<u>Experiment 3A</u>	1L/min N ₂	18M H ₂ SO ₄	18M H ₂ SO ₄	Empty [‡]	1M ROH	None
Micromoles HCN*		61.8	2.9	0.0 [‡]	<0.1	
% recovery [†]		95.5	4.5	--	<0.2	
<u>Experiment 3B</u>	1L/min N ₂	10% H ₂ SO ₄	18M H ₂ SO ₄	18M H ₂ SO ₄	Empty [‡]	1M KOH
Micromoles HCN*		13.2	151	13.6	0.0	<0.1
% recovery [†]		7.4	84.9	7.7	--	<0.1
<u>Experiment 3C</u>	0.6L/min N ₂ 0.4L/min CO ₂	18M H ₂ SO ₄	18M H ₂ SO ₄	Empty [‡]	1M KOH	None
Micromoles HCN*		257	55.9	0.0	<0.1	
% recovery [†]		82.4	17.6	--	<0.1	
<u>Experiment 3D</u>	1L/min 2% H ₂ S in N ₂	0.1M HCl	18M H ₂ SO ₄	18M H ₂ SO ₄	None	
Micromoles HCN*		1.8	53.1	4.9		
% recovery [‡]		3.0	87.2	8.0		

* Measured as NH₃ by Nesslerization

[†] Recovered NH₃ basis, input HCN not separately determined

[‡] To prevent entrained acid carryover to KOH impinger; no liquid was observed in the empty impinger after these experiments

[§] Input HCN was 60.9 micromoles; 98% total HCN recovery realized

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method, based upon GC analysis with a Hall detector, was employed with small volume bomb samples of this particular gas stream. The procedure is described in Section 9.1.3.

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APPENDIX B

IMPINGER PROCEDURE FOR SAMPLING OF AMMONIA AND CYANIDE

APPARATUS

The apparatus as shown in Figure A-1 consists of four 125 mL gas washing bottles with coarse cylindrical frits interconnected with Teflon lined Tygon tubing. A flow meter with a maximum flow of 1.25 L/min for the gases to be sampled is connected to the end of the train. The connections to the gas stream are all Teflon except for metering or shutoff valves which are of stainless steel. The inlet tube is connected to a tee which has metering/shutoff valves on the inlet side. One side is connected to a nitrogen tank and the other is connected via another tee to the stream to be sampled. Another shutoff/metering valve is connected to the open leg. The purpose of this leg is to allow the venting of gases before sampling is started.

PROCEDURE

Fill the first impinger with 25 mL 0.1N hydrochloric acid and the second and third impingers with 25 mL 98% sulfuric acid. Ammonia is trapped on the first impinger via an acid/base reaction with a selectivity of greater than 99%. Cyanide is trapped in the second and third impingers via a Lewis acid/base reaction and immediately hydrolyzed to ammonia. The fourth trap is to protect the flow meter from sulfuric acid mist and to smooth out perturbations in the flow caused by bubbling in the first three impingers. The impingers should be filled in an ammonia free environment preferably offsite in the laboratory, sealed, and shipped to the field for use.

Connect the train to both the gas stream to be sampled and the nitrogen bottle. Close all the valves. Pressurize the nitrogen line to 0.13 MPa and start a small flow of the gas stream to be sampled out of the vent. Make sure that these gases are safely vented. Open the nitrogen metering valve

slightly so that the sulfuric acid begins to be forced out of the first frit. Open the first impinger and hold the frit above the surface of the fluid until the acid is out of the frit. Close the impinger, secure the top, and repeat the procedure for the second impinger. Repeat for the third impinger. When all the impingers are bubbling at an even and stable rate, increase the flow to that desired for the test. When the system is stabilized, close the stream vent valve. Slowly open the stream input valve to the impingers. When an increase in flow is noticed, close the nitrogen valve to maintain a constant flow. Continue this process until the nitrogen valve is completely closed and the entire flow consists of the gas stream to be sampled. Sample for the required amount of time at a constant rate of flow.

When sampling is to be concluded, open the nitrogen valve until an increase in flow is noticed, then close the stream valve to maintain constant flow. Continue this process until the stream valve is closed and the entire flow through the impingers consists of nitrogen. Purge for at least five minutes. Slowly reduce the nitrogen to virtually zero. Do not close off the nitrogen valve. Open each impinger to release any residual pressure, starting with the last impinger. Close off the nitrogen valve, and close all impingers. Seal the input and output to the train, and clamp off the tubing between impingers in order to prevent cross contamination between impingers. Deliver the train to the laboratory for analysis.

Analysis of Impinger Solutions

Impinger solutions are determined using Method 417, Standard Methods for the Examination of Water and Wastewater, 15th Ed., 1980. Samples are neutralized and buffered at pH 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds. The sample is then distilled into a boric acid solution for analysis by Nesslerization or titration. The impinger samples consist of either 25-50 mL 0.1N HCl used to directly collect ammonia or 50-100 mL of conc. sulfuric acid used to collect and hydrolyze cyanide to ammonia. Carefully add either solution to 500 ml water in a two neck 1L flask attached to a Method 417 distillation apparatus. Be extremely careful to prevent localized overheating when the concentrated sulfuric acid is added to the water. Allow the solutions to cool before neutralization.

Analyze by the Nesslerization method, Method 417B. All the criteria of the general discussion must be met. If they are not, analyze by the titrimetric method, Method 417D. Many of the samples that must be analyzed have a high salt content and as a result will have a tendency to bump and destroy the apparatus. In order to avoid this problem, modify the distillation by using a heating mantle, a 2L 2-neck distillation flask and a slow nitrogen purge stream. This will insure smooth and stable boiling without bumping. Sensitivity is 2.5 μ mole.

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APPENDIX C

IMPINGER PROCEDURE FOR SAMPLING OF HYDROGEN CHLORIDE, HYDROGEN FLUORIDE, AND FORMIC ACID

APPARATUS

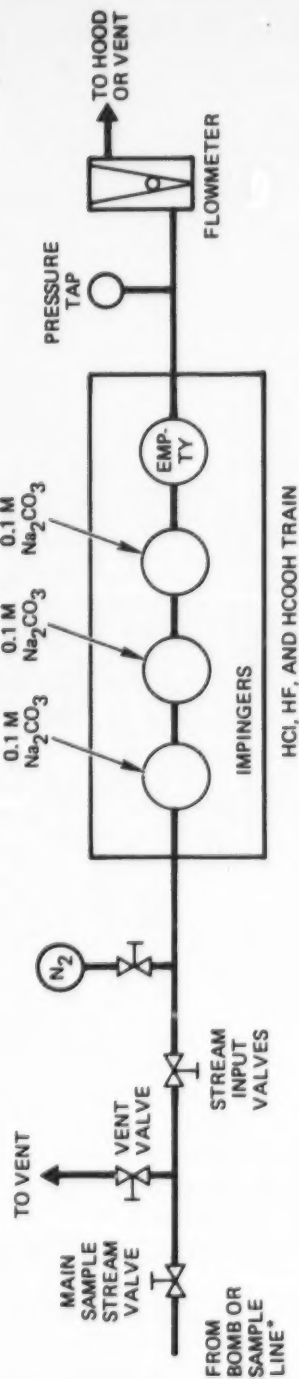
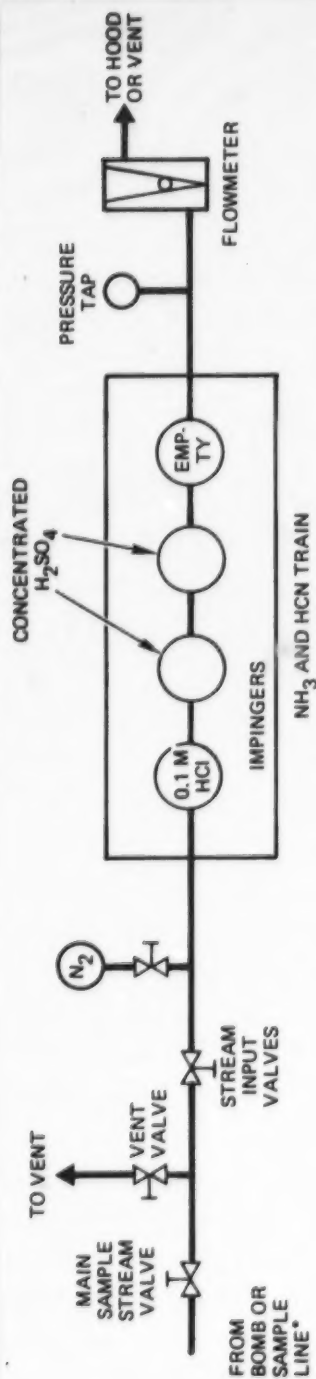
The apparatus as shown in Figure 8-1 consists of four 125 mL gas washing bottles with coarse cylindrical frits interconnected with Teflon lined Tygon tubing. A flow meter with a maximum flow of 125 L/min for the gases to be sampled is connected to the end of the train. The connections to the gas stream are all Teflon except for metering or shutoff valves which are of stainless steel. The inlet tube is connected to a tee which has metering/shutoff valves on the inlet side. One side is connected to a nitrogen tank and the other is connected via another tee to the stream to be sampled. Another shutoff/metering valve is connected to the open leg. The purpose of this leg is to allow the venting of gases before sampling is started.

PROCEDURE

Fill the first three impingers with 50 mL of a 0.1M sodium carbonate solution. Hydrogen chloride, hydrogen fluoride, and formic acid are trapped via acid base reaction while weaker acids such as hydrogen sulfide and carbon dioxide pass through without reaction. The third trap is to protect the flow meter from impinger mist and to smooth out perturbations in the flow caused by bubbling in the first three impingers. The impingers should be filled in an acid free environment preferably offsite in the laboratory, sealed, and shipped to the field for use.

Connect the train to both the gas stream to be sampled and the nitrogen bottle. Close all the valves. Pressurize the nitrogen line to 0.13 MPa and start a small flow of the gas stream to be sampled out of the vent. Make sure that these gases are safely vented. Open the nitrogen metering valve slightly so that the sulfuric acid begins to be forced out of the first frit.

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* IN THE LABORATORY A 7.6 L ALUMINUM BOMB IS ATTACHED TO EACH TRAIN

Figure C-1. HCl, HF, HCOOH, and HCN/NH₃ gas sampling trains configuration for on-site and laboratory gas collection

Open the first impinger and hold the frit above the surface of the fluid until all the acid is out of the frit. Close the impinger, secure the top, and repeat the procedure for the second impinger. When all the impingers are bubbling at an even and stable rate, increase the flow to that desired for the test. When the system is stabilized, close the stream vent valve. Slowly open the stream input valve to the impingers. When an increase in flow is noticed, close the nitrogen valve to maintain a constant flow. Continue this process until the nitrogen valve is completely closed and the entire flow consists of the gas stream to be sampled. Sample for the required amount of time at a constant rate of flow.

When sampling is to be concluded, open the nitrogen valve until an increase in flow is noticed, then close the stream valve to maintain constant flow. Continue this process until the stream valve is closed and the entire flow through the impingers consists of nitrogen. Purge for at least five minutes. Slowly reduce the nitrogen to virtually zero. Do not close off the nitrogen valve. Open each impinger to release any residual pressure, starting with the last impinger. Close off the nitrogen valve, and close all impingers. Seal the input and output to the train, and clamp off the tubing between impingers in order to prevent cross contamination between impingers. Deliver the train to the laboratory for analysis.

Procedure for the Determination of Formate, Chloride, and Fluoride in Impinger Samples

Formate, chloride, and fluoride in impinger samples are determined using a Dionex Model 16 ion chromatograph. The aqueous and impinger samples can be analyzed directly provided they do not need dilution or have a pH below 4 or above 8. In the case of extreme pH, suitable adjustment and/or dilution may be necessary. Empty the impingers into a 250 mL volumetric flask. Rinse each impinger, and add this material to the flask. Bring the solution to volume, and analyze directly.

Dionex Model 16 Ion Chromatographic Method for Formate --

Analyze for formate using the following instrumental conditions:

- Standard anion precolumn, separator, and suppressor
- Eluent - 0.005 M $\text{Na}_2\text{B}_4\text{O}_7$ (sodium borate)

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- Pump rate - 2.3 mL/min
- Injection volume - 100 μ L
- Full scale response - 30 μ S

Generate a calibration curve using formate standards of 1.0, 2.5, 5.0, and 10.0 ppm. A good calibration curve will have a correlation coefficient of 0.995 to 0.999. Run at least two blanks, one duplicate, and one spike per group of ten samples. Sensitivity is 0.1 ppm.

Dionex Model 16 Ion Chromatographic Method for Chloride and Fluoride --

Analyze for chloride and fluoride using the following instrumental conditions:

- Standard anion precolumn, separator, and suppressor
- Eluent - 0.003 M sodium bicarbonate, 0.0024 sodium carbonate
- Pump rate - 2.3 mL/min
- Injection volume - 100 μ L
- Full scale response - 30 μ S

Generate a calibration curve using a combined chloride/fluoride standard of 1.0, 2.5, 5.0, and 10.0 ppm. Good calibration curves will have correlation coefficients of 0.995 to 0.999. Run at least two blanks, one duplicate, and one spike per group of ten samples or less. Sensitivity is 0.1 ppm chloride; 0.1 ppm fluoride.

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- 1.1 This method covers the determination of those "unambiguous priority pollutants" associated with the Consent Decree that are solvent extractable and amenable to gas chromatography. The compounds listed in Tables 1 and 2 may be determined by this method.

TABLE 1**Base/Neutral Extractable Compounds**

COMPOUND	STORET NO.
acenaphthene	34205
acenaphthylene	34200
anthracene	34220
benzo(a)anthracene	34526
benzo(b)fluoranthene	34230
benzo(k)fluoranthene	34242
benzo(a)pyrene	34247
benzo(ghi)perylene	34521
benzidine	39120
bis(2-chloroethyl)ether	34273
bis(2-chloroethoxy)methane	34278
bis(2-ethylhexyl)phthalate	39100
bis(2-chloroisopropyl)ether	34283
4-bromophenyl phenyl ether	34636
butyl benzyl phthalate	34292
2-chloronaphthalene	34581
4-chlorophenyl phenyl ether	34641
chrysene	34320
dibenzo(a,h)anthracene	34556
di-n-butylphthalate	39110
1,3-dichlorobenzene	34566
1,4-dichlorobenzene	34571
1,2-dichlorobenzene	34536
3,3'-dichlorobenzidine	34631
diethylphthalate	34336
dimethylphthalate	34341
2,4-dinitrotoluene	34611
2,6-dinitrotoluene	34626
diethylphthalate	34596
1,2-diphenylhydrazine	34346
fluoranthene	34376
fluorene	34381
hexachlorobenzene	39700
hexachlorobutadiene	34391
hexachloroethane	34396
hexachlorocyclopentadiene	34386
indeno(1,2,3-cd)pyrene	34403
isophorone	34408
naphthalene	34696
nitrobenzene	34447
N-nitrosodimethylamine	34438
N-nitrosodi-n-propylamine	34428
N-nitrosodiphenylamine	34433
phenanthrene	34461
pyrene	34469
2,3,7,8-tetrachlorodibenzo-p-dioxin	34675
1,2,4-trichlorobenzene	34551

TABLE 2**Acid Extractable Compounds**

COMPOUND	STORET NO.
4-chloro-3-methylphenol	34452
2-chlorophenol	34586
2,4-dichlorophenol	34601
2,4-dimethylphenol	34606
2,4-dinitrophenol	34616
2-methyl-4,6-dinitrophenol	34657
2-nitrophenol	34591
4-nitrophenol	34646
pentachlorophenol	39094
phenol	34694
2,4,6-trichlorophenol	34621

- 1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the survey requirements of the Effluent Guidelines Division (EGD) and the National Pollutants Discharge Elimination System (NPDES).
- 1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Tables 3 and 4 represent the minimum quantity that must be injected into the system to get confirmation by the mass spectrometric method described below.
- 1.4 The GC-MS portions of this method are recommended for use only by analysts experienced with GC-MS or under the close supervision of such qualified persons.

2. SUMMARY OF METHOD

- 2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel or continuous extraction techniques. If emulsions are a problem, continuous extraction techniques should be used. The extract is dried over sodium sulfate and concentrated to a volume of 1 ± 0.1 ml using a Kuderna-Danish (K-D) evaporator. Chromatographic conditions are described which allow for the separation of the compounds in the extract.
- 2.2 Identification of a compound (qualitative analysis) is performed by an evaluation of background corrected characteristic ions.
- 2.3 Quantitative analysis is performed by GC-MS using isotope dilution.

APPENDIX E

METHOD 7 - DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

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1. Principle and Applicability

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams NO_x (as NO₂) per dry standard cubic meter, without having to dilute the sample.

2. Apparatus

2.1 Sampling (see Figure 7-1). Other grab sampling systems or equipment, capable of measuring sample volume to within ± 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within ± 5 percent, will be considered acceptable alternatives, subject to approval of the Administrator, U.S. Environmental Protection Agency. The following equipment is used in sampling:

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon[®] tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

*Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1° C (2° F) intervals from -5 to 50° C (25 to 125° F).

2.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm Hg (3 in. Hg) absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Vacuum Gauge. U-tube manometer, 1 meter (36 in.), with 1-mm (0.1-in.) divisions, or other gauge capable of measuring pressure to within ± 2.5 mm Hg (0.10 in. Hg).

2.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm Hg (3 in. Hg) absolute.

2.1.8 Squeeze Bulb. One-way.

2.1.9 Volumetric Pipette. 25 ml.

2.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-55 has been found to be effective.

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase, or vice versa for elevation decrease.

2.2 Sample Recovery. The following equipment is required for sample recovery:

2.2.1 Graduated Cylinder. 50 ml with 1-ml divisions.

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

2.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3 Analysis. For the analysis, the following equipment is needed:

2.3.1 Volumetric Pipettes. Two 1 ml, two 2 ml, one 3 ml, one 4 ml, two 10 ml, and one 25 ml for each sample and standard.

2.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallow-form, 195 ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150 ml), or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids

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should be removed by filtration (see Section 4.3).

2.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70° C (160° F) are acceptable alternatives.

2.3.4 Dropping Pipette or Dropper. Three required.

2.3.5 Polyethylene Policeman. One for each sample and each standard.

2.3.6 Graduated Cylinder. 100 ml with 1-ml divisions.

2.3.7 Volumetric Flasks. 50 ml (one for each sample and each standard), 100 ml (one for each sample and each standard, and one for the working standard KNO₃ solution), and 1000 ml (one).

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.

2.3.9 Graduated Pipette. 10 ml with 0.1-ml divisions.

2.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3.11 Analytical Balance. To measure to within 0.1 mg.

3. Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated H₂SO₄ to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery. Two reagents are required for sample recovery:

3.2.1 Sodium Hydroxide (1N). Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

3.2.2 Water. Deionized, distilled to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.3 Analysis. For the analysis, the following reagents are required:

3.3.1 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. **HANDLE WITH CAUTION.**

3.3.2 Phenol. White solid.

3.3.3 Sulfuric Acid. Concentrated, 95 percent minimum assay. **HANDLE WITH CAUTION.**

3.3.4 Potassium Nitrate. Dried at 105 to 110° C (220 to 230° F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.5 Standard KNO₃ Solution. Dissolve exactly 2.198 g of dried potassium nitrate (KNO₃) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1,000-ml volumetric flask.

3.3.6 Working Standard KNO₃ Solution. Dilute 10 ml of the standard solution to 100 ml with deionized distilled water. One milliliter of the working standard solution is equivalent to 100 µg nitrogen dioxide (NO₂).

3.3.7 Water. Deionized, distilled as in Section 3.2.2.

3.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100° C (212° F) for 2 hours. Store in a dark, stoppered bottle.

4. Procedures

4.1 Sampling.

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been properly greased with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position and turn the off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_f), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (V_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pres-

tures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO₂ (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N₂), then oxygen shall be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm Hg (3 in. Hg) absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample Recovery. Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1 N), dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis. Note the level of the liquid in container and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately prior to analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of deionized, distilled water. Add the rinse water to the flask and dilute to the

mark with deionized, distilled water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml deionized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with deionized, distilled water. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 5.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of deionized, distilled water if the absorbance exceeds A_c , the absorbance of the 400 μg NO₂ standard (see Section 5.2.2).

5. Calibration

5.1 Flask Volume. The volume of the collection flask-flask valve combination must be known prior to sampling. Assemble the flask and flask valve and fill with water, to the stopcock. Measure the volume of water to ± 10 ml. Record this volume on the flask.

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination. Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference

books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO, standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c . Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO₃ working standard solution (1 ml = 100 μg NO₂) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1 N) dropwise until the pH is between 9 and 12 (about 25 to 35 drops each). Dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 4.3 until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

Equation 7-1

where:

K_c = Calibration factor

A_1 = Absorbance of the 100- μg NO₂ standard

A_2 = Absorbance of the 200- μg NO₂ standard

A_3 = Absorbance of the 300- μg NO₂ standard

A_4 = Absorbance of the 400- μg NO₂ standard

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

5.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in 2.1.6.

5.6 Analytical Balance. Calibrate against standard weights.

6. Calculations

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

6.1 Nomenclature.

A = Absorbance of sample.

C = Concentration of NO, as NO₂, dry basis, corrected to standard conditions, mg/dscf (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration).

K_c = Spectrophotometer calibration factor.

m = Mass of NO, as NO₂, in gas sample, μg .

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_f = Final absolute temperature of flask, °K (°R).

T_i = Initial absolute temperature of flask, °K (°R).

T_{std} = Standard absolute temperature 293° K (528° R).

V_s = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

$2 = 50/25$, the aliquot factor. (If other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted).

6.2 Sample volume, dry basis, corrected to standard conditions.

$$V_{s,c} = \frac{T_{std}}{P_{std}} (V_f - V_a) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \\ = K_1 (V_f - 25 \text{ ml}) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

Equation 7-2

$$K_1 = 0.3858 \frac{^\circ\text{K}}{\text{mm Hg}} \text{ for metric units}$$

$$= 17.64 \frac{^\circ\text{R}}{\text{in. Hg}} \text{ for English units}$$

6.3 Total μg NO₂ per sample.

$$m = 2 K_c A F$$

Equation 7-3

Note.—If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

6.4 Sample concentration, dry basis, corrected to standard conditions.

$$C = K_2 \frac{m}{V_{s,c}}$$

Equation 7-4

where:

$$K_2 = 10^3 \frac{\text{mg/m}^3}{\mu\text{g/ml}} \text{ for metric units}$$

$$= 6.243 \times 10^{-3} \frac{\text{lb/scf}}{\mu\text{g/ml}} \text{ for English units}$$

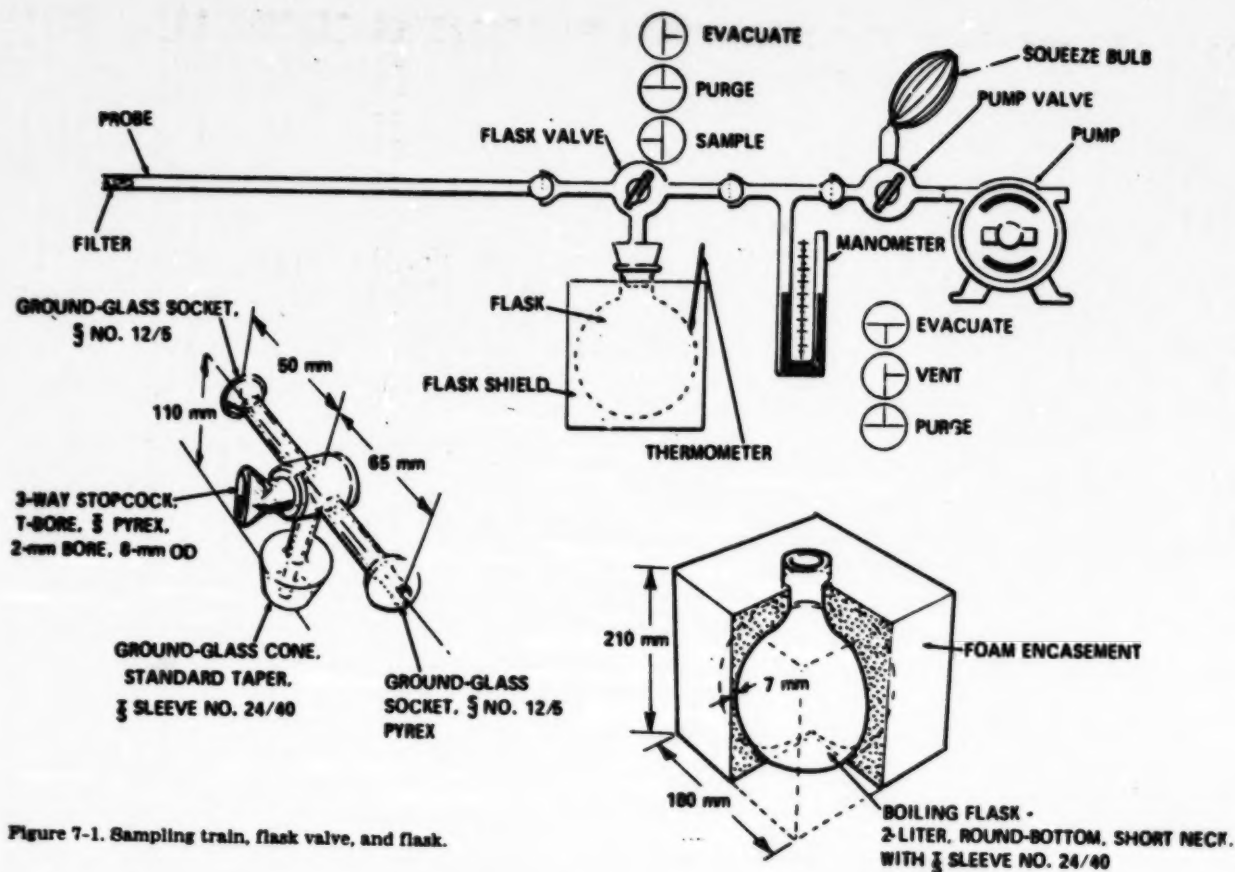


Figure 7-1. Sampling train, flask valve, and flask.

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METHOD 11 - DETERMINATION OF HYDROGEN SULFIDE CONTENT OF FUEL GAS STREAMS IN PETROLEUM REFINERIES

1. Principle and applicability. 1.1 *Principle.* Hydrogen sulfide (H_2S) is collected from a source in a series of midjet impingers and absorbed in pH 3.0 cadmium sulfate ($CdSO_4$) solution to form cadmium sulfide (CdS). The latter compound is then measured iodometrically. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species. This method is a revision of the H_2S method originally published in the *FEDERAL REGISTER*, Volume 39, No. 47, dated Friday, March 8, 1974.

1.2 *Applicability.* This method is applicable for the determination of the hydrogen sulfide content of fuel gas streams at petroleum refineries.

2. Range and sensitivity. The lower limit of detection is approximately 8 mg/m^3 (6 ppm). The maximum of the range is 740 mg/m^3 (520 ppm).

3. Interferences. Any compound that reduces iodine or oxidizes iodide ion will interfere in this procedure, provided it is collected in the cadmium sulfate impingers. Sulfur dioxide in concentrations of up to 2,600 mg/m^3 is eliminated by the hydrogen peroxide solution. Thiols precipitate with hydrogen sulfide. In the absence of H_2S , only co-traces of thiols are collected. When methane- and ethane-thiols at a total level of 300 mg/m^3 are present in addition to H_2S , the results vary from 2 percent low at an H_2S concentration of 400 mg/m^3 to 14 percent high at an H_2S concentration of 100 mg/m^3 . Carbon oxysulfide at a concentration of 20 percent does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring end points. However, acetaldehyde and acetone at concentrations of 1 and 3 percent, respectively, do not interfere.

Entrained hydrogen peroxide produces a negative interference equivalent to 100 percent of that of an equimolar quantity of hydrogen sulfide. Avoid the ejection of hydrogen peroxide into the cadmium sulfate impingers.

4. Precision and accuracy. Collaborative testing has shown the within-laboratory coefficient of variation to be 2.2 percent and the overall coefficient of variation to be 5 percent. The method bias was shown to be -4.8 percent when only H_2S was present. In the presence of the interferences cited in section 3, the bias was positive at low H_2S concentration and negative at higher concentrations. At 230 $mg H_2S/m^3$, the level of the compliance standard, the bias was +2.7 percent. Thiols had no effect on the precision.

5. Apparatus.

5.1 Sampling apparatus.

5.1.1 Sampling line. Six to 7 mm ($\frac{1}{4}$ in.) Teflon¹ tubing to connect the sampling train to the sampling valve.

5.1.2 Impingers. Five midjet impingers, each with 30 ml capacity. The internal diameter of the impinger tip must be 1 mm $\pm$ 0.05 mm. The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

5.1.3 Glass or Teflon connecting tubing for the impingers.

5.1.4 Ice bath container. To maintain absorbing solution at a low temperature.

¹Mention of trade names of specific products does not constitute endorsement by the Environmental Protection Agency.

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5.1.5 Drying tube. Tube packed with 8- to 16-mesh indicating-type silica gel, or equivalent, to dry the gas sample and protect the meter and pump. If the silica gel has been used previously, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Administrator.

NOTE.—Do not use more than 30 g of silica gel. Silica gel absorbs gases such as propane from the fuel gas stream, and use of excessive amounts of silica gel could result in errors in the determination of sample volume.

5.1.6 Sampling valve. Needle valve or equivalent to adjust gas flow rate. Stainless steel or other corrosion-resistant material.

5.1.7 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate (~1.0 liter/min) and conditions actually encountered during sampling. The meter shall be equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3° C (5.4° F). The gas meter should have a petcock, or equivalent, on the outlet connector which can be closed during the leak check. Gas volume for one revolution of the meter must not be more than 10 liters.

5.1.8 Flow meter. Rotameter or equivalent, to measure flow rates in the range from 0.5 to 2 liters/min (1 to 4 cfh).

5.1.9 Graduated cylinder, 25 ml size.

5.1.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice-versa for elevation decrease.

5.1.11 U-tube manometer, 0-30 cm water column. For leak check procedure.

5.1.12 Rubber squeeze bulb. To pressurize train for leak check.

5.1.13 Tee, pinchclamp, and connecting tubing. For leak check.

5.1.14 Pump. Diaphragm pump, or equivalent. Insert a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter. The pump is used for the air purge at the end of the sample run; the pump is not ordinarily used during sampling, because fuel gas streams are usually sufficiently pressurized to force sample gas through the train at the required flow rate.

The pump need not be leak-free unless it is used for sampling.

5.1.15 Needle valve or critical orifice. To set air purge flow to 1 liter/min.

5.1.16 Tube packed with active carbon. To filter air during purge.

5.1.17 Volumetric flask. One 1,000 ml.

5.1.18 Volumetric pipette. One 15 ml.

5.1.19 Pressure-reduction regulator. Depending on the sampling stream pressure, a pressure-reduction regulator may be needed to reduce the pressure of the gas stream entering the Teflon sample line to a safe level.

5.1.20 Cold trap. If condensed water or amine is present in the sample stream, a corrosion-resistant cold trap shall be used immediately after the sample tap. The trap shall not be operated below 0° C (32° F) to avoid condensation of C₁ or C₂ hydrocarbons.

5.2 Sample recovery.

5.2.1 Sample container. Iodine flask, glass-stoppered; 500 ml size.

5.2.2 Pipette, 50 ml volumetric type.

5.2.3 Graduated cylinders. One each 25 and 250 ml.

5.2.4 Flasks, 125 ml, Erlenmeyer.

5.2.5 Wash bottle.

5.2.6 Volumetric flasks. Three 1,000 ml.

5.3 Analysis.

5.3.1 Flask, 500 ml glass-stoppered iodine flask.

5.3.2 Burette, 50 ml.

5.3.3 Flask, 125 ml, Erlenmeyer.

5.3.4 Pipettes, volumetric. One 25 ml; two each 50 and 100 ml.

5.3.5 Volumetric flasks. One 1,000 ml; two 500 ml.

5.3.6 Graduated cylinders. One each 10 and 100 ml.

6. Reagents. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use best available grade.

6.1 Sampling.

6.1.1 Cadmium sulfate absorbing solution. Dissolve 41 g of 3CdSO₄·8H₂O and 15 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately ¾ liter of deionized distilled water. Dilute to volume with deionized water. Mix thoroughly. pH should be 3±0.1. Add 10 drops of Dow-Corning Antifoam B. Shake well before use. If Antifoam B is not used, the alternate acidified iodine extraction procedure (section 7.2.2) must be used.

6.1.2 Hydrogen peroxide, 3 percent. Dilute 30 percent hydrogen peroxide to 3 percent as needed. Prepare fresh daily.

6.1.3 Water. Deionized, distilled to conform to ASTM specifications D1193-72, Type 3. At the option of the analyst, the KMnO₄ test for oxidizable organic matter may be omitted when high concentrations

of organic matter are not expected to be present.

6.2 Sample recovery.

6.2.1 Hydrochloric acid solution (HCl), 3M. Add 240 ml of concentrated HCl (specific gravity 1.19) to 500 ml of deionized, distilled water in a 1-liter volumetric flask. Dilute to 1 liter with deionized water. Mix thoroughly.

6.2.2 Iodine solution 0.1 N. Dissolve 24 g of potassium iodide (KI) in 30 ml of deionized, distilled water. Add 12.7 g of resublimed iodine (I_2) to the potassium iodide solution. Shake the mixture until the iodine is completely dissolved. If possible, let the solution stand overnight in the dark. Slowly dilute the solution to 1 liter with deionized, distilled water, with swirling. Filter the solution if it is cloudy. Store solution in a brown-glass reagent bottle.

6.2.3 Standard iodine solution, 0.01 N. Pipette 100.0 ml of the 0.1 N iodine solution into a 1-liter volumetric flask and dilute to volume with deionized, distilled water. Standardize daily as in section 8.1.1. This solution must be protected from light. Reagent bottles and flasks must be kept tightly stoppered.

6.3 Analysis.

6.3.1 Sodium thiosulfate solution, standard 0.1 N. Dissolve 24.8 g of sodium thiosulfate pentahydrate ($Na_2S_2O_5 \cdot 5H_2O$) or 15.8 g of anhydrous sodium thiosulfate ($Na_2S_2O_5$) in 1 liter of deionized, distilled water and add 0.01 g of anhydrous sodium carbonate (Na_2CO_3) and 0.4 ml of chloroform ($CHCl_3$) to stabilize. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 minutes and store in a glass-stoppered, reagent bottle. Standardize as in section 8.1.2.

6.3.2 Sodium thiosulfate solution, standard 0.01 N. Pipette 50.0 ml of the standard 0.1 N thiosulfate solution into a volumetric flask and dilute to 500 ml with distilled water.

NOTE.—A 0.01 N phenylarsine oxide solution may be prepared instead of 0.01 N thiosulfate (see section 6.3.3).

6.3.3 Phenylarsine oxide solution, standard 0.01 N. Dissolve 1.80 g of phenylarsine oxide (C_6H_5AsD) in 150 ml of 0.3 N sodium hydroxide. After settling, decant 140 ml of this solution into 800 ml of distilled water. Bring the solution to pH 6-7 with 6N hydrochloric acid and dilute to 1 liter. Standardize as in section 8.1.3.

6.3.4 Starch indicator solution. Suspend 10 g of soluble starch in 100 ml of deionized,

distilled water and add 15 g of potassium hydroxide (KOH) pellets. Stir until dissolved, dilute with 900 ml of deionized distilled water and let stand for 1 hour. Neutralize the alkali with concentrated hydrochloric acid, using an indicator paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.

NOTE.—Test starch indicator solution for decomposition by titrating, with 0.01 N iodine solution, 4 ml of starch solution in 200 ml of distilled water that contains 1 g potassium iodide. If more than 4 drops of the 0.01 N iodine solution are required to obtain the blue color, a fresh solution must be prepared.

7. Procedure.

7.1 Sampling.

7.1.1 Assemble the sampling train as shown in figure 11-1, connecting the five midjet impingers in series. Place 15 ml of 3 percent hydrogen peroxide solution in the first impinger. Leave the second impinger empty. Place 15 ml of the cadmium sulfate absorbing solution in the third, fourth, and fifth impingers. Place the impinger assembly in an ice bath container and place crushed ice around the impingers. Add more ice during the run, if needed.

7.1.2 Connect the rubber bulb and manometer to first impinger, as shown in figure 11-1. Close the petcock on the dry gas meter outlet. Pressurize the train to 25-cm water pressure with the bulb and close off tubing connected to rubber bulb. The train must hold a 25-cm water pressure with not more than a 1-cm drop in pressure in a 1-minute interval. Stopcock grease is acceptable for sealing ground glass joints.

NOTE.—This leak check procedure is optional at the beginning of the sample run, but is mandatory at the conclusion. Note also that if the pump is used for sampling, it is recommended (but not required) that the pump be leak-checked separately, using a method consistent with the leak-check procedure for diaphragm pumps outlined in section 4.1.2 of reference method 6, 40 CFR Part 60, Appendix A.

7.1.3 Purge the connecting line between the sampling valve and first impinger, by disconnecting the line from the first impinger, opening the sampling valve, and allowing process gas to flow through the line for a minute or two. Then, close the sampling valve and reconnect the line to the impinger train. Open the petcock on the dry gas meter outlet. Record the initial dry gas meter reading.

7.1.4 Open the sampling valve and then adjust the valve to obtain a rate of approximately 1 liter/min. Maintain a constant (± 10 percent) flow rate during the test. Record the meter temperature.

7.1.5 Sample for at least 10 min. At the end of the sampling time, close the sampling valve and record the final volume and temperature readings. Conduct a leak check as described in Section 7.1.2 above.

7.1.6 Disconnect the impinger train from the sampling line. Connect the charcoal tube and the pump, as shown in figure 11-1. Purge the train (at a rate of 1 liter/min) with clean ambient air for 15 minutes to ensure that all H_2S is removed from the hydrogen peroxide. For sample recovery, cap the open ends and remove the impinger train to a clean area that is away from sources of heat. The area should be well lighted, but not exposed to direct sunlight.

7.2 Sample recovery.

7.2.1 Discard the contents of the hydrogen peroxide impinger. Carefully rinse the contents of the third, fourth, and fifth impingers into a 500 ml iodine flask.

NOTE.—The impingers normally have only a thin film of cadmium sulfide remaining after a water rinse. If Antifoam B was not used or if significant quantities of yellow cadmium sulfide remain in the impingers, the alternate recovery procedure described below must be used.

7.2.2 Pipette exactly 50 ml of 0.01 N iodine solution into a 125 ml Erlenmeyer flask. Add 10 ml of 3 M HCl to the solution. Quantitatively rinse the acidified iodine into the iodine flask. Stopper the flask immediately and shake briefly.

7.2.2 (Alternate). Extract the remaining cadmium sulfide from the third, fourth, and fifth impingers using the acidified iodine solution. Immediately after pouring the acidified iodine into an impinger, stopper it and shake for a few moments, then transfer the liquid to the iodine flask. Do not transfer any rinse portion from one impinger to another; transfer it directly to the iodine flask. Once the acidified iodine solution has been poured into any glassware containing cadmium sulfide, the container must be tightly stoppered at all times except when adding more solution, and this must be done as quickly and carefully as possible. After adding any acidified iodine solution to the iodine flask, allow a few minutes for absorption of the H_2S before adding any further rinses. Repeat the iodine extraction until all cadmium sulfide is removed from the impingers. Extract that part of the connecting glassware that contains visible cadmium sulfide.

Quantitatively rinse all of the iodine from the impingers, connectors, and the beaker into the iodine flask using deionized, dis-

tilled water. Stopper the flask and shake briefly.

7.2.3 Allow the iodine flask to stand about 30 minutes in the dark for absorption of the H_2S into the iodine, then complete the titration analysis as in section 7.3.

NOTE.—Caution! Iodine evaporates from acidified iodine solutions. Samples to which acidified iodine have been added may not be stored, but must be analyzed in the time schedule stated in section 7.2.3.

7.2.4 Prepare a blank by adding 45 ml of cadmium sulfate absorbing solution to an iodine flask. Pipette exactly 50 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl. Follow the same impinger extracting and quantitative rinsing procedure carried out in sample analysis. Stopper the flask, shake briefly, let stand 30 minutes in the dark, and titrate with the samples.

NOTE.—The blank must be handled by exactly the same procedure as that used for the samples.

7.3 Analysis.

NOTE.—Titration analyses should be conducted at the sample-cleanup area in order to prevent loss of iodine from the sample. Titration should never be made in direct sunlight.

7.3.1 Using 0.01 N sodium thiosulfate solution (or 0.01 N phenylarsine oxide, if applicable), rapidly titrate each sample in an iodine flask using gentle mixing, until solution is light yellow. Add 4 ml of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V_{T_1} , the volume of sodium thiosulfate solution used, or V_{A_1} , the volume of phenylarsine oxide solution used (ml).

7.3.2 Titrate the blanks in the same manner as the samples. Run blanks each day until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml.

8. Calibration and standards.

8.1 Standardizations.

8.1.1 Standardize the 0.01 N iodine solution daily as follows: Pipette 25 ml of the iodine solution into a 125 ml Erlenmeyer flask. Add 2 ml of 3 M HCl. Titrate rapidly with standard 0.01 N thiosulfate solution or with 0.01 N phenylarsine oxide until the solution is light yellow, using gentle mixing. Add four drops of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V_T , the volume of thiosulfate solution used, or V_{A_2} , the volume of phenylarsine oxide solution used (ml). Repeat until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml and calculate the exact normality of the iodine

solution using equation 9.3. Repeat the standardization daily.

8.1.2 Standardize the 0.1 N thiosulfate solution as follows: Oven-dry potassium dichromate ($K_2Cr_2O_7$) at 180 to 200° C (360 to 390° F). Weigh to the nearest milligram, 2 g of potassium dichromate. Transfer the dichromate to a 500 ml volumetric flask, dissolve in deionized, distilled water and dilute to exactly 500 ml. In a 500 ml iodine flask, dissolve approximately 3 g of potassium iodide (KI) in 45 ml of deionized, distilled water, then add 10 ml of 3 M hydrochloric acid solution. Pipette 50 ml of the dichromate solution into this mixture. Gently swirl the solution once and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of deionized distilled water, washing down the sides of the flask with part of the water. Titrate with 0.1 N thiosulfate until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record V_s , the volume of thiosulfate solution used (ml). Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using equation 9.1. Repeat the standardization each week, or after each test series, whichever time is shorter.

8.1.3 Standardize the 0.01 N Phenylarsine oxide (if applicable) as follows: oven dry potassium dichromate ($K_2Cr_2O_7$) at 180 to 200° C (360 to 390° F). Weigh to the nearest milligram, 2 g of the $K_2Cr_2O_7$; transfer the dichromate to a 500 ml volumetric flask, dissolve in deionized, distilled water, and dilute to exactly 500 ml. In a 500 ml iodine flask, dissolve approximately 0.3 g of potassium iodide (KI) in 45 ml of deionized, distilled water; add 10 ml of 3M hydrochloric acid. Pipette 5 ml of the $K_2Cr_2O_7$ solution into the iodine flask. Gently swirl the contents of the flask once and allow to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of deionized, distilled water, washing down the sides of the flask with part of the water. Titrate with 0.01 N phenylarsine oxide until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record V_a , the volume of phenylarsine oxide used (ml). Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using equation 9.2. Repeat the standardization each week or after each test series, whichever time is shorter.

8.2 Sampling train calibration. Calibrate the sampling train components as follows:

8.2.1 Dry gas meter.

8.2.1.1 Initial calibration. The dry gas meter shall be calibrated before its initial use in the field. Proceed as follows: First, assemble the following components in series: Drying tube, needle valve, pump, rotameter, and dry gas meter. Then, leak-check the system as follows: Place a vacuum gauge (at least 760 mm Hg) at the inlet to the drying

tube and pull a vacuum of 250 mm (10 in.) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

Next, calibrate the dry gas meter (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet test meter (e.g., 1 liter per revolution) to the inlet of the drying tube. Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the dry gas meter is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

8.2.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in section 8.2.1.1. above, except for the following variations: (a) The leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in section 8.2.1.1.), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the dry gas meter as in section 8.2.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

8.2.2 Thermometers. Calibrate against mercury-in-glass thermometers.

8.2.3 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

8.2.4 Barometer. Calibrate against a mercury barometer.

9. Calculations. Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

9.1 Normality of the Standard (~0.1 N) Thiosulfate Solution.

$$N_s = 2.039W/V_s$$

where:

W = Weight of $K_2Cr_2O_7$ used, g.

V_s = Volume of $Na_2S_2O_3$ solution used, ml.

N_s = Normality of standard thiosulfate solution, g-eq/liter.

2.039 = Conversion factor

(6 eq. L/mole $K_2Cr_2O_7$) (1,000 ml/liter)/
(294.2 g $K_2Cr_2O_7$ /mole) (10 aliquot factor)

9.2 Normality of Standard Phenylarsine Oxide Solution (if applicable).

$$N_A = 0.2039 W/V_A$$

where:

W = Weight of $K_2Cr_2O_7$ used, g.
 V_A = Volume of C_6H_5AsO used, ml.
 N_A = Normality of standard phenylarsine oxide solution, g-eq/liter.
 0.2039 = Conversion factor

(6 eq. L/mole $K_2Cr_2O_7$) (1,000 ml/liter)/
(249.2 g $K_2Cr_2O_7$ /mole) (100 aliquot factor)

9.3 Normality of Standard Iodine Solution.

$$N_I = N_I V_I / V_I$$

where:

N_I = Normality of standard iodine solution, g-eq/liter.
 V_I = Volume of standard iodine solution used, ml.
 N_T = Normality of standard (~0.01 N) thiosulfate solution; assumed to be 0.1 N_A g-eq/liter.
 V_T = Volume of thiosulfate solution used, ml.

NOTE.—If phenylarsine oxide is used instead of thiosulfate, replace N_T and V_T in Equation 9.3 with N_A and V_A , respectively (see sections 8.1.1 and 8.1.3).

9.4 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C) and 760 mm Hg.

$$V_{std} = V_m Y [(T_{std}/T_m) (P_{bar}/P_{std})]$$

where:

V_{std} = Volume at standard conditions of gas sample through the dry gas meter, standard liters.
 V_m = Volume of gas sample through the dry gas meter (meter conditions), liters.
 T_{std} = Absolute temperature at standard conditions, 293° K.
 T_m = Average dry gas meter temperature, °K.
 P_{bar} = Barometric pressure at the sampling site, mm Hg.
 P_{std} = Absolute pressure at standard conditions, 760 mm Hg.
 Y = Dry gas meter calibration factor.

9.5 Concentration of H_2S . Calculate the concentration of H_2S in the gas stream at standard conditions using the following equation:

$$C_{H_2S} = KI(V_I N_I - V_T N_T) \text{ sample} - (V_I N_I - V_T N_T) \text{ blank} / V_{std}$$

where (metric units):

C_{H_2S} = Concentration of H_2S at standard conditions, mg/dscm.

K = Conversion factor = 17.04×10^3

(34.07 g/mole H_2S) (1,000 liters/m³) (1,000 mg/g)/(1,000 ml/liter) (2 H_2S eq/mole)

V_I = Volume of standard iodine solution = 50.0 ml.

N_I = Normality of standard iodine solution, g-eq/liter.

V_T = Volume of standard (~0.01 N) sodium thiosulfate solution, ml.

N_T = Normality of standard sodium thiosulfate solution, g-eq/liter.

V_{std} = Dry gas volume at standard conditions, liters.

NOTE.—If phenylarsine oxide is used instead of thiosulfate replace N_T and V_T in Equation 9.5 with N_A and V_A , respectively (see Sections 7.3.1 and 8.1.3).

10. Stability. The absorbing solution is stable for at least 1 month. Sample recovery and analysis should begin within 1 hour of sampling to minimize oxidation of the acidified cadmium sulfide. Once iodine has been added to the sample, the remainder of the analysis procedure must be completed according to sections 7.2.2 through 7.3.2.

11. Bibliography.

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11.2 Tentative Method of Determination of Hydrogen Sulfide and Mercaptan Sulfur in Natural Gas, Natural Gas Processors Association, Tulsa, Okla., NGPA Publication No. 2265-65, 1965.

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11.4 Schell, G. W., and M. C. Sharp. Standardization of Method 11 at a Petroleum Refinery, Midwest Research Institute Draft Report for USEPA, Office of Research and Development, Research Triangle Park, N.C. 27711, EPA Contract No. 68-02-1098, August 1976, EPA 600/4-77-088a (Volume 1) and EPA 600/4-77-088b (Volume 2).

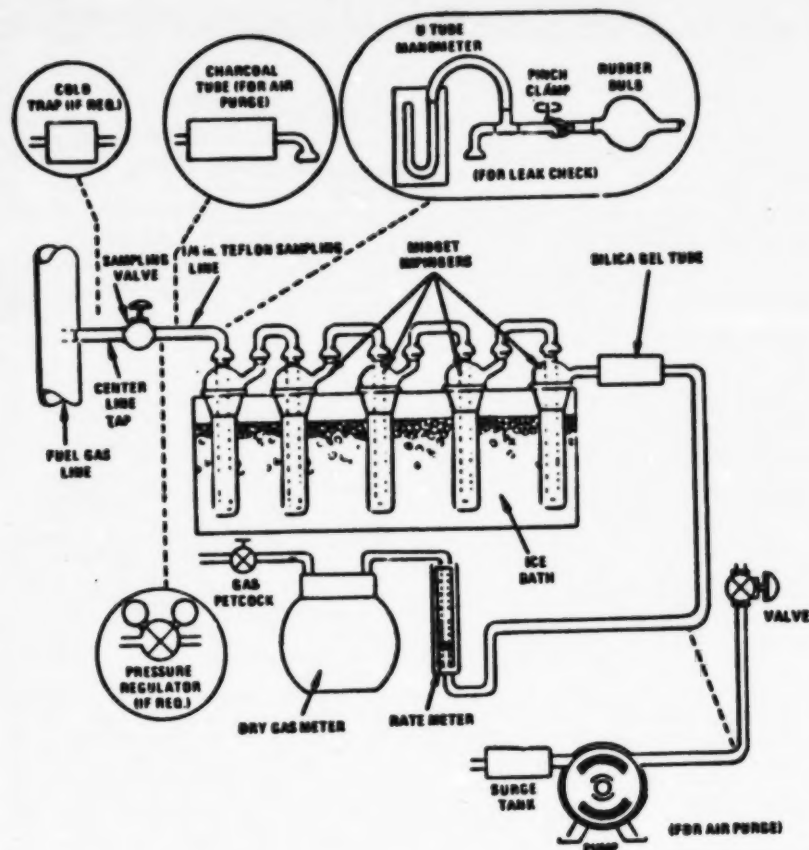


Figure F-1. H₂S sampling train

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APPENDIX G

METHOD 15 - DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE EMISSIONS FROM STATIONARY SOURCES

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INTRODUCTION

The method described below uses the principle of gas chromatographic separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent usable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the criteria set below are met.

1. Principle and applicability

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) by gas chromatographic (GC) separation and flame photometric detection (FPD).

1.2 Applicability. This method is applicable for determination of the above sulfur compounds from tail gas control units of sulfur recovery plants.

2. Range and sensitivity

2.1 Range. Coupled with a gas chromatographic system utilizing a 1-milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppm. It may be necessary to dilute gas samples from sulfur recovery plants hundred-fold (99:1) resulting in an upper limit of about 1000 ppm for each compound.

2.2 The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppm for a 1 ml sample.

3. Interferences

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effects on the flame photometric detector even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting CO and CO_2 before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO, in the diluent gas. The CO level should be approximately 10 percent for the case with CO, present. The two chromatographs should show agreement within the precision limits of section 4.1.

3.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling line can lead to eventual coating and even blockage of the sample line. This problem can be eliminated along with the moisture problem by heating the sample line.

4. Precision

4.1 Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than ± 13 percent from the mean of the three injections.

4.2 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period shall not exceed ± 5 percent.

5. Apparatus

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.2 The sample line must be made of Teflon,¹ no greater than 1.3 cm (1/2 in) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120° C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120° C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert material (e.g. stainless steel or Teflon). It must be heated to 120° C and be capable of approximately a 9:1 dilution of the sample.

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature $\pm 1^\circ$ C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature $\pm 1^\circ$ C.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.3.4 Flame Photometric Detector.

5.3.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.3.4.2 Power Supply. Capable of delivering up to 750 volts.

5.3.4.3 Recorder. Compatible with the output voltage range of the electrometer.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H_2S , COS , and CS_2 .

To demonstrate that adequate resolution has been achieved the tester must submit a chromatograph of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable

¹Mention of trade names or specific products does not constitute an endorsement by the Environmental Protection Agency.

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AND ILLUSTRATIONS

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standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero ± 5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5.1 Calibration System. The calibration system must contain the following components.

5.5.2 Flow System. To measure air flow over permeation tubes at ± 2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within $\pm 1.1^\circ\text{C}$.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within $\pm 1^\circ\text{C}$.

6. Reagents

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

6.5 Calibration Gases. Permeation tubes, one each of H_2S , COS , and CS_2 , gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7. Pretest Procedures

The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8. Calibration

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components; particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the

tubes within $\pm 0.1^\circ\text{C}$. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K \times P / ML$$

Equation 15-1

where:

C = Concentration of permeant produced in ppm.

P = Permeation rate of the tube in $\mu\text{g}/\text{min}$.

M = Molecular weight of the permeant: g/g-mole.

L = Flow rate, l/min, of air over permeant @ 20°C , 760 mm Hg.

K = Gas constant at 20°C and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of analysis system. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injections for each concentration must yield the precision described in section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data.

8.5 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration

data for H_2S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of section 4.1 are still applicable.

9. Sampling and Analysis Procedure

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. Post-Test Procedures

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ± 20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is

unacceptable. Sampling losses of 0-20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in section 8. Only H₂S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. Calculations

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least squares line.

11.2 Calculation of SO₂ Equivalent. SO₂ equivalent will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during the given analysis.

$$\text{SO}_2 \text{ equivalent} = \Sigma(\text{H}_2\text{S}, \text{COS}, 2 \text{CS}_2)d$$

Equation 15-2

where:

SO₂ equivalent = The sum of the concentration of each of the measured compounds (COS, H₂S, CS₂) expressed as sulfur dioxide in ppm.

H₂S = Hydrogen sulfide, ppm.

COS = Carbonyl sulfide, ppm.

CS₂ = Carbon disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average SO₂ equivalent will be determined as follows:

$$\text{Average SO}_2 \text{ equivalent} = \frac{\sum \text{SO}_2 \text{ equiv.}_i}{N(1 - \text{Bwo})}$$

Equation 15-3

where:

Average SO₂ equivalent = Average SO₂ equivalent in ppm, dry basis.

Average SO₂ equivalent = SO₂ in ppm as determined by Equation 15-2.

N = Number of analyses performed.

Bwo = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases (36 FR 24887).

12. Example System

Described below is a system utilized by EPA in gathering NSPS data. This system does not now reflect all the latest developments in equipment and column technology, but it does represent one system that has been demonstrated to work.

12.1 Apparatus.

12.1.1 Sample System.

12.1.1.1 Probe. Stainless steel tubing, 6.35 mm (1/4 in.) outside diameter, packed with glass wool.

12.1.1.2 Sample Line. 1/8 inch inside diameter Teflon tubing heated to 120° C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120° C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 15-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120° C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyer Teflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent per dilution stage. A 9:1 dilution of sample is accomplished by combining 150 cc of sample with 1350 cc of clean dry air as shown in Figure 15-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120° C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min. ±1 percent per dilution stage.

12.1.3.0 Gas Chromatograph.

12.1.3.1 Column—1.83 m (6 ft.) length of Teflon tubing, 2.16 mm (0.085 in.) inside diameter, packed with deactivated silica gel, or equivalent.

12.1.3.2 Sample Valve. Teflon six port gas sampling valve, equipped with a 1 ml sample

loop, actuated by compressed air (Figure 15-1).

12.1.3.3 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100° C, constant within $\pm 1^\circ$ C.

12.1.3.4 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature $\pm 1^\circ$ C.

12.1.3.5 Flow System. Gas metering system to measure sample flow, hydrogen flow, oxygen flow and nitrogen carrier gas flow.

12.1.3.6 Detector. Flame photometric detector.

12.1.3.7 Electrometer. Capable of full scale amplification of linear ranges of 10^{-2} to 10^{-4} amperes full scale.

12.1.3.8 Power Supply. Capable of delivering up to 750 volts.

12.1.3.9 Recorder. Compatible with the output voltage range of the electrometer.

12.1.4 Calibration. Permeation tube system (Figure 15-3).

12.1.4.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.4.2 Mass Flowmeters. Two mass flowmeters in the range 0-3 l/min. and 0-10 l/min. to measure air flow over permeation tubes at ± 2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter at least once each year.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30° C within $\pm 0.1^\circ$ C.

12.2 Reagents.

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in section 8.3.

12.2.5 Compressed Air. 80 psig for GC valve actuation.

12.2.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at 30.0° C.

12.3 Operating Parameters. The operating parameters for the GC/FPD system are as follows: nitrogen carrier gas flow rate of 100 cc/min, exhaust temperature of 110° C, detector temperature 105° C, oven temperature of 40° C, hydrogen flow rate of 80 cc/minute, oxygen flow rate of 20 cc/minute, and sample flow rate of 80 cc/minute.

12.4 Analysis. The sample valve is actuated for 1 minute in which time an aliquot of diluted sample is injected onto the separation column. The valve is then deactivated for the remainder of analysis cycle in which time the sample loop is refilled and the separation column continues to be foreflushed. The elution time for each compound will be determined during calibration.

13. Bibliography

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